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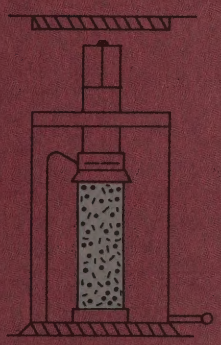

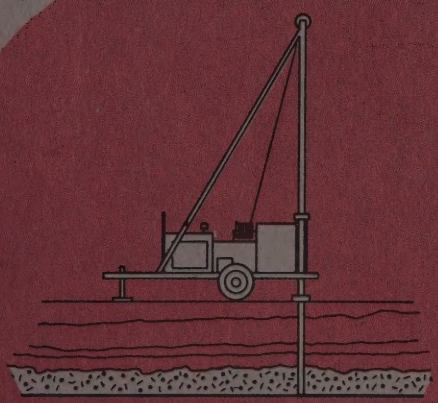

"PHYSICO-CHEMICAL PROPERTIES OF SOIL-WATER SYSTEMS"

A SERIES OF LECTURES BY
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at the

BUREAU OF SOIL MECHANICS
N.Y. STATE DEPARTMENT OF TRANSPORTATION
ALBANY, N.Y.

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SYLLABUS

"Physico-Chemical Properties of Soil-Water Systems"

A series of lectures by
Professor Hans F. Winterkorn
Princeton University

March 9, 10, 11 and April 13, 14, 15, 1970

at the

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0. Selected constants, egnations, and glossary, as well as outlines of topics.

I. Major topics treated March 9 - 11.

1. Soils and soil problems in highway engineering. What is soil? What is soil engineering? What is pedology and how can it help the engineer? Geology and the soil engineer. Thermodynamics and its pertinence to soil engineering.

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2. Application of the laws of physics to particulate systems. The molecular and macromeritic solid, liquid, and gaseous states; application to mechanical resistance properties of soil systems. Friction and cohesion. Soils with and without granular bearing skeleton.

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3. The peculiar properties of the water substance explained by the structure of the H_2O-molecule; the structure of the soil minerals. Interaction between water and soil minerals. Water and soil minerals as oxygen - ion structures.

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4. The physical meaning of the Atterberg limits and other soil properties. The scientific principles underlying the various engineering soil classifications.

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5. Movement of water in soil under hydraulic, electric and thermal gradients. Darcy flow, electroosmosis, thermo-osmosis. Engineering applications.

Page 18 - HYDRAULIC
Page 21 - ELECTRIC
Page 23 - THERMAL

6. The scientific basis of soil stabilization. Granulometric and physico-chemical principles.

II. Major topics treated April 13, 14, 15.

7. Soil and heat. Heat capacities and coefficients of thermal conduction of the common solid, liquid and gaseous phases of soils; heats of wetting; change of water affinity with temperature. Bulk heat conduction in soils and contribution of various conducting mechanisms. The daily and yearly temperature wave in surface soil layers and its engineering consequences.

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Page 51 - PROBLEMS OF MOISTURE MOVEMENT UNDER THERMAL GRADIENT

8. Aerial wells and water accumulation in highway bases and subgrades; also capillarity and frost action.

9. Granulometric principles and the design of drainage skeleton.

10. The stabilization of soils with a granular bearing skeleton.

11. Physico-chemical properties and engineering behavior of cohesive soils.

12. The stabilization of cohesive soils without a granular bearing skeleton.

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0. Selected units and constants

F = Force: ma = mlt^{-2}-dyne (cgs-system)

E = Energy-work: Fl = ml^2t^{-2}-erg (cgs-system)

10^7 erg = 1 joule
1 cal = 4.185 joule
1 kcal = 4185 joule
1 electron volt: 1 ev = 1.602×10^{-12} erg = 0.386×10^{-19} cal.
Avogadro number = 6.02×10^{23}
R-gas constant = 1.987 cal/mol °C
= 0.082 liter atmosphere/mol °C.
h-Planck constant = 6.62×10^{-27} erg seconds
e-electron charge = 4.803×10^{-10} (erg. cm)$^{\frac{1}{2}}$ also (esu)
= 1.6×10^{-19} Coulomb.

Acquiring facility to calculate with atomic and molecular mass-, force-, and energy units

Energy and strength values for ionic crystals

Example: Na CL
1. Electrostatic assumption: Force = $\frac{e_o^2}{\Delta^2}$

2. Madeling reduction because of influence of all other ions in crystal: Force = $0.2905 \frac{e_o^2}{\Delta^2}$

3. Work to break one bond: $Wb = 0.2905 \frac{e_o^2}{\Delta_o}$

4. Refinement by Born and Lande: $Wb = \frac{(8)}{(9)} (0.2905) \frac{e_o^2}{\Delta_o}$

5. Selection of value for Δ_o

(a) sum of ionic radii from x-ray diffraction

$r_{Na^+} + r_{Cl^-} = 0.98 + 1.81 = \underline{2.79}$ ANGSTROM

(b) $\Delta_o = \sqrt[3]{\frac{M}{2N_A \cdot \rho}}$ in which: M = mole weight = 58.5
N_A = 6.02 x 10^{23}
ρ = density of Na Cl = 2.15 g/cm^3

$= \underline{2.827 \times 10^{-8} cm}$

$\underline{\text{chosen} = 2.81 \times 10^{-8} cm}$

6. Work to break one bond: $Wb = 0.258 \frac{e_o^2}{\Delta_o} = \frac{0.258 (4.8)^2 (10)^{-20}}{2.81 \times 10^{-8}}$

$Wb = 2.13 \times 10^{-12}$ erg

7. Tensile Strength - TS

$TS = \frac{(1)}{(3)} \frac{Wb}{\Delta_o^3} \equiv \frac{2.13 \times 10^{-12}}{3(2.81)^3 \times 10^{-24}} = \frac{0.71}{22.7} \times 10^{12}$ dyne/cm^2

$= 3.2 \times 10^{10}$ dyne/cm^2 = 3.2 x 10^4 kg/cm^2 = 45.5x10^4 psi

Note: common TS valves of NaCl determined in air are about 50 kg/cm^2; in saturated NaCl solution valves range from 2.4 to 7 x 10^3 kg/cm^2.

8. Surface energy and surface tension from tensile strength with simple triangular assumption for variation of bond strength with distance.

$\frac{TS \times \Delta_o}{2}$ = 2 x surface energy (Ws)/cm^2

$$W_s = \frac{(1)}{(4)} 3.2 \times 10^{10} \times 2.8 \times 10^{-8} = 224 \text{ erg/cm}^2$$

In the cgs system surface tension is numerically equal to surface energy per unit surface.
Note: Eucker, Stern, and Born calculated about 150 erg/cm^2; experimentally obtained valves are about 300 erg/cm^{-2}.

9. Lattice energy: $E_L = \frac{(6)}{(2)} 2 N_A \times W_b$

$= (6) 6.02 \times 10^{23} \times 2.13 \times 10^{-12}$

$= 77.2 \times 10^{11}$ erg

$= 184$ kcal

OUTLINES OF LECTURES AND DISCUSSION TOPICS

I 1. Soils and Soil Problems in Highway Engineering

Definitions of soil: engineering, geologic, pedologic

Pedology, the natural science of soil formation, composition and behavior has three branches: (1) soil genesis, (2) soil classification, (3) soil mapping; all three are useful to the soil engineer. Why?

Geology, furnishes the parent material or substrata for soil genesis.

A soil or a soil characteristic is a function of the soil forming factors: parent material, climate, topography, organisms (including man), and time.

Thermodynamics contains the supreme physical laws which all happenings on earth must obey -

(a) equilibrium thermodynamics: FIRST;SECOND; & THIRD LAW;
(b) irreversible reactions - rate processes - activation theory.

ENGINEERING FUNCTION	ENGINEERING PROBLEM
Loading of the soil	Bearing capacity; soil-structure interaction
Soil as construction material	Soil technology; soil stabilization
Soil as a loading material	Earth pressure
Medium on which vehicles move	Trafficability, off-road mobility
Medium on which water moves	Erosion; bed load movement
Medium through which water moves	Seepage, drainage, water resources
et alia	et alia

I2. Application of the Laws of Physics to Particulate Systems

(1) Character of soil as a polyphase, multicomponent system and character of soil engineering problems gives pertinence to all common subdivisions of physics as indicated below:

SUBDIVISION OF PHYSICS	SOIL ENGINEERING EXAMPLES
Mechanics	Soil Mechanics problems
Electricity & Magnetism	Electro-osmosis; electrochemical soil stabilization;
Thermodynamics	Heat capacity and transmission properties; heats of wetting, heats of reaction with stabilizers; thermoelectric effects; heats of activities for physical and chemical rate processes;
Acustics and generally transmission of mechanical vibratory energy	Earthquake shock and damage as related to soils and soil condition; effect of machine vibration an foundations; testing with explosives and mechanical vibrators;
Optics	Soil color as an important index; reflection, refraction, and absorption of electro magnetic energy
Chemical Physics	Soil-water interaction, soil-stabilizer interaction, etc.
Nuclear Physics	Use of Neutrons for H_2O determination and of x-rays for density; protective function of soil against nuclear blast.

(2) The Collumeritic Concept

All material systems--gases, liquids, solids, and combinations and composites--represent assemblies of particles that are either independent of each other (ideal gases) reaching only to mutual impact, or are subject to attraction and bonding forces of greater or lesser magnitude.

(a) In the case of ideal gases obeying the molar gase law PV=RT, the total content in kinetic translatory energy of the component 6.02×10^{23} molecules is (3/2) RT or (3/2) kT per molecule where k = Boltzmann constant. Considering only perfectly elastic collisions and conservation of both energy and momentum, the (3/2 kT per molecules exerts a dispersing effect counteracting what attracting forces may exist between two molecules. From the kinetic energy of a gas molecule, we can calculate its velocity since (3/2) kT = $\frac{mv^2}{2}$. Accordingly:

$$\sqrt{\bar{v}^2} = \sqrt{\frac{3RT}{M}}$$

where M = molecular weight, R = Gas Constant, T = absolute temperatures or in cgs - units:

$$\overline{v^2} = 15790 \sqrt{\frac{T}{M}} \text{ cm/sec (square root of mean } [v^2])$$

$$\bar{v} = 14540 \sqrt{\frac{T}{M}} \text{ cm/sec (average velocity)}$$

$$v_m = 12900 \sqrt{\frac{T}{M}} \text{ cm/sec (velocity possessed by largest number of molecules)}$$

$$v_m = \frac{\sqrt{\pi}}{2} \cdot \bar{v} = \frac{2}{3} \overline{v^2}$$

What bearing do these velocities have on the type of atmosphere possessed by a celestial body?

Examples of bond forces between atoms and molecules.

Type of Bond	Pair	Length in ANGSTROM	Energy of Bond k cal/mol	erg/bond	ev
Ionic	Na^+F^-	1.88	157	109×10^{-11}	6.18
Ion-Dipole	$Na(OH_2)$	2.14	21.6	1.5×10^{-12}	0.93
Dipole-Dipole	H_2O-H_2O	2.37	4.84	3.37×10^{-13}	0.208
Dispersion	Ne^2-Ne	3.30	0.06	4.27×10^{-15}	0.0026

ADSORPTION ENERGIES & LINGERING TIMES

Heat of Adsorption in k cal/mol	Lingering time in seconds
1.5	1.3×10^{-12}
3.5	4×10^{-11}
4.0	1×10^{-10}
10	3.2×10^{-6}
15	1.8×10^{-2}
20	1×10^{-2}
25	about 1 week
30	more than 100 years

I 3. THE PECULAIR PROPERTIES OF THE WATER SUBSTANCE

Properties of the water substance

Formula	H_2O	Surface Tension(18°C)	72.8 dyne
Mole Weight	18.015	Viscosity(η) x 10^2 (18°C)	1.05
Refractive Index	1.333	Specific Heat	0.999 cal/g
Specific Gravity	1.00	Heat of Fusion	79.7 cal/g
Melting Point(1 atm)	0°C	Heat of Evapor.(100°C)	539.1 cal/g
Boiling Point(1 atm)	100°C	Critical Temperature	374°C
D= Dielectric Constant (18°C)	81	Critical Pressure	156 atm

= Dipole Moment 1.7 - 1.87 x 10^{-18} esu

$\frac{D-1}{D+2}\frac{M}{S} = \frac{4\pi N_A}{3}\left(\alpha + \frac{\mu^2}{3kt}\right)$ - What is physical meaning of this equation?

Some of the Peculiar Properties of Water

(1) High melting and boiling temperatures:

Substance	Mole Weight	Boiling Temp. °C
H_2O	18	100
H_2S	34	-62
H_2Se	81	-42
H_2Te	130	-4

(2) Negative coefficient of volume change up to 4°C

(3) Melting temperature decreases with increase in pressure, to 2200 kg/cm^2, then increases to 81.6°C at 22000 kg/cm^2.

(4) Formation of gas hydrates at temperatures above normal melting points.

(5) High specific heat of 1 cal/g and 18 cal/mol.

Water should be a gas, is a liquid, and has certain properties that are typical of solids. Why?

What is water volumetrically?

Considering the volume of a water molecule as essentially equal to that of an O^{2-} ion, then 6.02×10^{23} molecules have a "solid" volume of about 6.62 cm^3. For various packings the following mole volumes are obtained:

(0) absolute solid volume of one mole	6.6 cm^3
(1) hexagonal rhombohedric packing	8.94 "
(2) tetragonal spheroidal packing	9.49 "
(3) orthorhombic packing	10.92 "
(4) cubic (regular) packing	12.64 "
(5) liquid H_2O	18.00 "
(6) ice (normal)	19.65 "

Porority of normal water = (18.0 - 6.6)/18 = 0.633 = 63.3%
" " " ice = (19.65 - 6.6)/19.65 = 0.664 = 66.4%

This looseness is typical of a tetrahedral arrangement of 4 equal sized atoms or ions around a central one of the same size. This structure is also possessed by diamond.

Other important tetrahedral group - $(Si\ O_4)^{4-}$

Much denser because of small size of Si^{4+}
Volume percent of Si^{4+} and O^{2-} in solid SiO_2 is Si^{9+} = 1.29% and O^{2-} = 98.7%: neglecting volume of Si^{4+} we find for mole volume of O^{2-} in 3 enantiotropic forms of SiO_2 the following:

Mineral	Spec. Gravity	Mole Volume of O^{2-}	Porosity %
Tridymite	2.28	13.1	49.6
Cristobalite	2.32	12.9	48.8
Quartz	2.65	11.3	41.6
Coesite	2.90	10.3	35.9

Soil Minerals essentially O^{2-} - structures

Mineral	% solid ion volume O^{2-}	% solid ion volume Si^{4+}	Volume per mole of O^{2-}	Formula
ORTHOCLASE	87.2	0.86	13.4-13.7	$KALSi_3O_8$
ALBITE	93.2	0.92		$NaAeSi_3O_8$
MUSCOVITE	89.9	0.95	10.75-12.0	$KH_2Ae_3Si_3O_{12}$

Crystalline clays are layer minerals consisting volumetraically mainly of O^{2-} and OH^- ions arranged tetrahedrally around Si^{4+} ions and octahedrally around Al^{3+} and Mg^{2+} ions (as well as others of approximately the same size).
Lack of internal electric equilibrium due to substitution of ions of lower valency for some of higher valency leads to charge transfer to particle surfaces and to phenomenon to cation exchange capacity. Important is not only the total number of such charges per unit weight of soil but also the structure of the ensuing electric field.

Water is also essentially an O^{2-} - structure - hence the easy and multiforious interaction of water with the surface of soil minerals.

Interaction of soil mineral surfaces and water

(a) Amount of surface per unit solid volume as a function of particle size: surface/volume = $\frac{3}{r}$ (spheres) or $\frac{6}{d}$ (cubes)

Material	d in cm	surface in cm^2/cm^3
Gravel	8 - 0.2	0.75 - 30
Sand	0.2 - 0.0005	30 - 1200
Silt	0.005-0.0005	1200 - 12,000
Clay	0.0005-0.0001	12,000 - 60,000
Colloids	0.0001	>60,000

(b) geometric and electric surface features;
(c) type and number of exchange ions
(d) geometry of water molecule and of its dissociation products: H^+, OH^-, and O^{2-}.

Types of water found in SOIL-WATER SYSTEMS

(1) in solid solution in mineral surface
(2) wall-effect or "ice-berg" water
(3) ion hydratation or "electorstricted" water
(4) osmotic water
(5) free water
(6) air-water interface and meniscus water.

TENSILE STRENGTH OF WATER

$$TS = \frac{4\sigma}{\Delta_o} = \frac{4 \times 75}{3.1 \times 10^{-8}} \text{ dyne/cm}^2$$

$$TS = \frac{300}{3.1} \times 10^8 = 96.6 \times 10^8 \text{ dyne/cm}^2$$

$$\Delta_o = \sqrt[3]{\frac{M}{N_A \cdot S}} = \sqrt[3]{\frac{18}{6.02 \times 10^{23}}}$$

$$= 3.107 \times 10^{-8} \text{ cm}$$

$$TS = 0.986 \times 10^4 \text{ kg/cm}^2$$

$$TS = 14 \times 10^4 \text{ psi}$$

TS (calculated by KORNFELD from internal pressure derived from pressure-volume function) = 3.25×10^3 Kg/cm^2

TS (highest measured value in centrifuge method) = 280 kg/cm^2

I 4. THE PHYSICAL MEANING OF THE ATTERBERG LIMITS AND OTHER SOIL PROPERTIES

(1) Size categories of particulate soil components

(a) larger than openings of #200 sieve (74μ) - granular, sand, gravel, cobbles etc.

(b) smaller than 74μ- silt-clay material, governing interaction with water and properties such as cohesion, plasticity, swelling, shrinkage, et alia.

The +#200 material should be submitted to sieve analysis preferably with same set as used for Abrams FINENESS MODULUS, thus utilizing experience from concrete technology.

The Atterberg and other water-interaction tests should be made on the -#200 (silt-clay) material instead of (or addition to) on the -#40 (420μ) material.

(2) Two general categories of disturbed, compacted soils:

(a) those with granular bearing skeleton,

(b) those without granular bearing skeleton.

Dividing line is silt-clay content whose volume together with that of water at plastic limit exceeds pore volume of the densified +#200 fraction.

(3) Pore volume of the granular fraction is function of size range, gradation, and angularity of particles as illustrated in attached figure.

(4) The physical meaning of Atterberg and other tests derives is defined by the test procedure rather than by the name chosen for the test. Discuss this with respect to:

Hygroscopicity
Liquid and plastic limits
Plasticity index
Field moisture equivalent
Vacuum moisture equivalent
Centrifuge moisture equivalent
Shrinkage limit
Heat of wetting
Sorption of liquids and swelling
on hand of the data in attached tables.

FIGURE 3

RELATION BETWEEN NORMAL POROSITY AND SIZE RANGE AS EXPRESSED BY D_{MAX}/D_{MIN} IN CONTINUOUS GRADING.

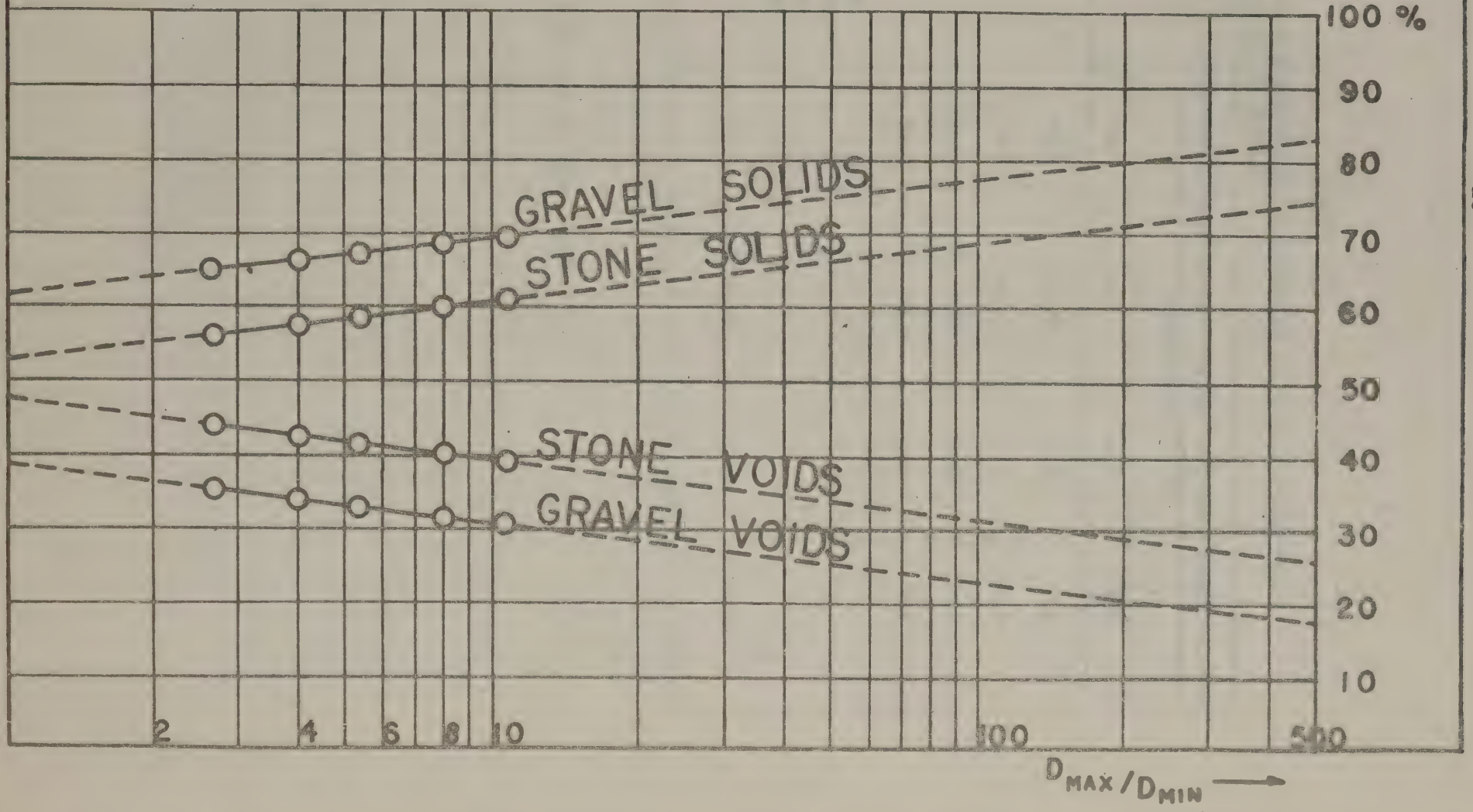


Table 5.7

Hygroscopicity as a Function of Temperature at Constant H_2O-vapor Pressure of 30 mm Hg at 30°C.[1)]

Clay Type	Hygroscopicity in percent H_2O per dry weight of soil			
	Temperature in °C			
	30°	40°	50°	80°
H - Bentonite	32.7	13.0	7.5	2.1
H - Putnam	25.8	10.8	5.7	2.3
H - Davidson	21.4	3.5	2.6	1.2
H - Permutite	28.4	16.9	4.9	3.1
Concentration of H_2SO_4 - H_2O mixture used to maintain constant humidity				
Percent H_2SO_4	10	41.5	52.75	68.75

1) Soil Science, Vol. 40, p. 411 , 1935

Table 5+8

Relationship Between Hygroscopicity and Other Properties for Several Types of Hydrogen-Clays[1)]

Property	Type of H-Clay				
	Bentonite	Lufkin	Putnam	Susquehanna	Cecil
Type of mineral	Montmorillonite	Montmorillonite Beidellite	Beidellite	Beidellite Halloysite	Holloysite
$SiO_2 - R_2O_3$ ratio	5.0	3.8	3.2	2.3	1.3
Exchange capacity m. ./100 g	95.0	82.0	65.0	47.0	13.0
Hygroscopicity % (30% H_2SO_4)	21.5	20.1	18.1	15.5	6.1
Heat of Wetting cal/g of clay	16	15.0	13.8	11.7	5.9
Hygroscopicity Heat of Wetting	1.34	1.34	1.31	1.32	1.03
Hygroscopicity Exchange Capacity	0.22	0.24	0.28	0.33	0.47
Swelling cc H_2O/g of soil	2.2	1.18	0.81	0.57	0.05
Swelling Heat of Wetting	0.14	0.08	0.06	0.05	0.01

[1)] H. F. Winterkorn, "Studies on the Surface Behavior of Bentonites and Clays", Soil Science, Vol. 41, No. 1; pp. 25-32, 1936.

Table 5-9

Effect of Type of Exchange Ion on the Hygroscopicity and Other Properties of Putnam Clay.[1)]

Property	Type of Exchange Ion					
	H^+	Li^+	Na^+	K^+	Ca^{++}	Ba^{++}
Hygroscopicity (a) 30% H_2SO_4	18.13	17.13	16.53	12.75	17.37	16.29
(b) 3.3% H_2SO_4	44.76	56.12	49.22	31.12	40.97	41.95
Heat of Wetting cal/g clay	13.6	12.0	12.0	9.5	15.0	13.9
Hygroscopicity (a) Heat of Wetting	1.33	1.43	1.38	1.34	1.16	1.17
Swelling cc H_2O/ g clay	2.2	10.77	11.08	8.85	2.5	2.5
Swelling Heat of Wetting	0.06	0.41	0.34	0.05	0.06	0.06

[1)] L. D. Baver and Hans F. Winterkorn: Sorption of Liquids by Soil Colloids II. Soil Science, Vol. 40, No. 5; pp. 403-419, 1935.

Table 5.10

Test Constants of Typical Fine-Grained Materials[1)]

Material	Grading		Consistency			Shrinkage	
	Effective Size in microns	Uniformity Coefficient	Liquid limit	Plastic limit	Plasticity index	Limit	Ratio
Bentonite	0.2	3.2	399	45	354	6	2.2
Diatoms	0.3	9.1	136	115	21	125	0.6
Mica	2.3	9.1	116		0	165	0.6
Muck	0.3	7.0	112	39	73	33	1.4
Zinc oxide	0.1	2.4	89	35	54	31	1.9
Clay soil	0.2	8.8	80	29	51	13	1.9
Pumice	6.6	5.0	52		0	57	1.0
Kaolin	0.4	11.0	43	28	15	37	1.3
Talc	2.8	7.5	36	25	11	29	1.4
Quartz flour	2.1	19.1	18		0	26	1.6

1) After C. A. Hogentogler "Engineering Properties of Soils", McGraw-Hill Book Company, Inc., Page 234, 1937.

I 5. MOVEMENT OF WATER IN SOIL UNDER HYDRAULIC, ELECTRIC AND THERMAL GRADIENTS

(1) HYDRAULIC GRADIENTS

Darcy equation for unit cross section

$\frac{dV}{dt} = ki$ in which $\frac{dV}{dt}$ = volume yield rate of flow

k = transmission constant

i = hydraulic gradient

Poiseville equation for capillary flow

$\frac{dVc}{dt} = \frac{\pi r^4}{8\eta} i = \frac{\pi r^2 \cdot r^2}{8\eta} i$ in which r = radius of capillary

η = viscosity of liquid

Replacing actual soil cross section by one containing m capillaries of radius r, then

$\frac{dV}{dt} = m \frac{dV_c}{dt} = \frac{m\pi r^2 . r^2}{8\eta} i$ and $k = \frac{m\pi r^2 . r^2}{8\eta}$

Multiplying top and bottom of last equation with unit length gives

$k = \frac{n \cdot r^2}{8\eta l}$ since $m \pi r^2 l$ equals porosity n.

considering $\frac{r^2}{4} = \left(\frac{r^2\pi}{2r\pi}\right)^2 = \left(\frac{\text{cross section}}{\text{wetted perimeter}}\right)^2 = \left(\frac{\text{porosity}}{\text{internal surface}}\right)^2 =$

$= \left(\frac{n}{s_i}\right)^2$; hence

$K = \frac{n}{2\eta}\left(\frac{n}{s_i}\right)^2$ - For illustration of use of this equation See Table I

Table I

Interrelationships between Grain Size, Capillary Rise, Internal Surface, Porosity, and Hydraulic Permeability of Granular Soil Systems[1)]

(a) Grain Sizes			(b)	(c)	(d)	(e)	(f) (g) Coefficient of Hydraulic Permeability k in 10^{-4} cm/sec.	
Passing Sieve No.	Retained Sieve No.	Average Diameter in cm.	Saturated Capillary Rise in cm.	Surface per cm^3 Solid in $cm.^2$	Surface per cm^3 Pore Vol. from Cap. Rise Data	Porosity Calculated from (c) and (d)	Experimental	Calculated from Data in Columns (d) and (e)
10	20	0.118	6.4	51	85.4	37.5	50	23
20	30	0.069	9.4	81	125	39.3	23	13
30	40	0.049	13.2	122	176	41.0	13	6.6
40	60	0.031	20.0	194	267	41.0	6.7	2.7
60	80	0.021	29.8	290	397	42.3	5.7	1.3
80	100	0.016	35.6	370	475	43.8	2.7	0.97
100	140	0.012	47.0	488	628	43.8	1.6	0.55
140	200	0.0087	67.0	690	894	43.5	0.7	0.27
200	270	0.0062	90.5	970	1210	44.4	0.3	0.15

1) Experimental data for grain size, capillary rise and permeability from Highway Research Board Bulletin 209 on Subsurface Drainage of Highways and Airports, 1959.

Condition of state for molecular systems depends on relative magnitude of dispersive--temperature dependent kinetic--and attractive--or bonding--forces:
gaseous--dispersion $\gg$ mutual attraction
liquid--dispersion $\approx$ mutual attraction
solid --dispersion $\ll$ mutual attraction

Volume relationships between solid, liquid, and gaseous states of simple chemical components.

V Solid :V Liquid :V Liquid = 1:1.21:1.42
($0^{\circ}K$) (MP) (B.P. 1 atm.)

ANALOGIES BETWEEN MOLECULAR AND MACRO MERITIC SYSTEMS

Critical void ratios in sand and gravel correspond to molecular melting point volumes;
Coefficient of friction in sand and gravel systems follows similar volume law as coefficient of viscoeity in liquids where mole volumes are functions of temperature.
Multicomponent macromeritic systems behave similar to multi-component molecular systems.
(See pertinent publications by Winterkorn, Kezdi, and other).

Cohesion in Soil System
(a) time cohesion due to molecular bonding forces
(b) surface tension cohesion due to presence of water-air interfaces in moist soil systems
(later discussion in greater detail.)

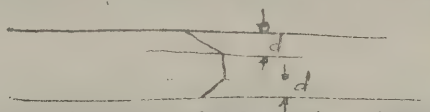
(2) ELECTRIC POTENTIAL GRADIENT ELECTRO-OSMOSIS

HELMHOLTZ assumptions for flow in capillary at applied electric potential gradient E:

1. Very (but not infinitesimally) thin electric double layer formed by one type of charges in solid wall and the opposite in vicinal liquid at distance d;

2. The first molecular layer of the liquid vicinal to the wall is immobil and has velocity zero;

3. The flow velocity builds up with distance from wall to v at the thickness d of the double layer whence the velocity v remains constant resulting in a plug type flow in the capillary:



4. The wall is an insulator while the liquid has electric conductivity:

Assume further:

(a) e = electric charge on capillary wall per cm length

(b) The electric double layer system acts like a cylindrical condenser of capacity $C = \frac{Dr}{2d}$ in which D = dielectric constant, r=radius of capillary, and d=thickness of double layer; $e/C = \emptyset$=potential of the double layer; $e = \emptyset/C = \emptyset\ (Dr/2d)$

(c) Electric driving force $F_e = eE = \emptyset\ \frac{Dr}{2d}.E$

(d) Viscous resistance to flow in double layer $Fr = S\eta \frac{\Delta v}{\Delta r}$ where

S = wall surface for 1 cm length = $2r\pi$ x 1 cm^2

$\frac{\Delta v}{\Delta r}$ = flow velocity within double layer to maximum value of v = velocity of plug flow: hence $\Delta v/\Delta r = v/d$;
$F_r = 2r\pi\eta(v/d)$

(e) for steady flow: $F_e = F_r$ or $\emptyset \frac{Dr}{2d} .E = 2r\pi\eta \frac{v}{d}$

flow velocity $v = \frac{D\emptyset E}{4\pi\eta}$ and volume flow rate $\frac{dV}{dt} = v.r^2\pi$

$$\frac{dV}{dt} = \frac{D\emptyset r^2\pi}{4\pi\eta} .E$$

(f) for a unit cross section containing m capillaries of cross section $r^2\pi$ we get $m.r^2\pi$ = porosity n, hence k_e = electro-osmotic transmission coefficeint = $\frac{nD\emptyset}{4\pi\eta}$

What can and should be said about D $\emptyset$ and η valves in such systems.

Other Approaches to Understanding of Electro-osmosis Assume that electric charge is due to exchange cations present in soil-water system; electric driving force per unit soil volume is cations in pore liquid times gradient E, also assume Poiseuville type flow:

Example:

Clay: Sp.G. 2.6; CEC = 20 me/100g,
saturated with 50 volume percent H_2O.

Hence: 1.3g clay/cc of system, having electric charge per cm^3 of
$1.3 \times \frac{0.02}{100} \times 96500 - 25$ coulombs/cm^3

1 volt/cm applied to 1 coulomb exerts force of 10^7 dyne or about 10^4g equal to a head of 10^4 cm of water; hence 1 volt/cm applied to the soil system is equivalent to a hydraulic gradient of 25×10^4 cm/cm

Placing this into previously developed equation:

$\frac{dV}{dt} = \frac{n}{2\eta\ell} \left(\frac{n}{s}\right)^2 . i$ - taking S = 77,000 cm^2/g of soil and $k_{DARCY} = 6.25 \times 10^{-10}$ cm/sec -

we obtain for the electroosmotic transmission coefficient:

$k_s = 6.25 \times 10^{-10} \times 25 \times 10^4 = 1.56 \times 10^{-4}$ cm/sec per volt/cm.

Compare this with velocity of ions in water at 18°C in field of 1 volt/cm, expressed in units of 10^{-4} cm/sec:

ION	K+	Ag+	Na+	Li+	H+	OH-	Cl-	NO_3-
VELOCITY	6.67	5.6	4.43	3.45	32.4	17.8	6.76	6.4

We may further assume that the electric charges per unit soil volume are proportional to the internal soil surface present. Putting liquid viscosity and geometric factors into a constant C we may write: $k_e = C \frac{n^3}{s^2} \times s = C \frac{n^3}{s}$;

Since the solid surface $s = C' (1-n)^{2/3}$, we may write $k_e = C'' (n^3 / (1-n)^{2/3}$; why?

Thermo-osmotic Flow

WATER MOVEMENT IN SOIL-WATER SYSTEM UNDER THERMAL GRADIENT

Several mechanisms of water transfer in liquid, film, and gas phases contribute depending on soil and phase composition of system. Maximum possible efficiency can be calculated from Second Law of thermodynamics and system properties. See ASTM Spec. Techn. Publication 163. pp 27-35, 1954.

Soil-Heat Relationships

The Nature of Heat

Heat is a form of energy. As in the case of other forms of energy, a definite amount of heat can be expressed as the product of a capacity and an intensity factor. The former is the heat capacity, the latter the absolute temperature. The heat capacity per gram of a given material is called its specific heat, that for the atomic weight in grams is the atomic heat and that for a gram mol of a compound is the molecular heat. The total heat content U of a system possessing the heat capacity C and being at an absolute temperature T is expressed by

$$U = \int_0^T C\,dt \qquad 9.1$$

where C itself is a function of temperature.

The concept of heat as a form of motion of the ultimate particulate components of matter goes back to the ancients. Scientific proof for its essential correctness was obtained mainly during the last century. But even at the present time, scientists and engineers do not realize all the implications of this concept with respect to their every day work. The heat capacity of the ultimate particulate components depends primarily on their degrees of freedom, i.e. their ability to utilize kinetic energy or to store it as potential energy. Thus, the molecules of monoatomic gases can utilize kinetic energy only by moving in the three dimensions of space and possess accordingly only three degrees of freedom. In full development, each degree of

freedom utilizes an amount of energy per gram mol of RT/2 where R is the gas constant. Hence, the atomic heat of such gases is 3 R/2 or about 3 calories. Diatomic molecules add, to the three possible translatory movements, rotations around two major axes which results in a mol heat of 5 R/2, while molecules with more atoms may have three axes of rotation, bringing the mol heats to 6 R/2. At elevated temperatures interatomic vibrations within the molecules become mobilized and result in increased heat capacities. At still higher temperatures, electronic energy utilization becomes important.

The experimental law of Dulong and Petit according to which the atomic heats tend to lie in the vicinity of 6 R/2 for solids is explained by the freedoms of vibration in the three dimensions of space whereby 2 R/2 are assigned to each vibrational freedom, because both kinetic and potential energies are involved. It is not surprizing that a theory based on such simple assumptions has its definite limitations. Rather, it is amazing, how much can be done with a few simple assumptions based, of course, on experimental and other observations and their logical mathematical development.

The mechanical heat theory holds well for ideal gases and dilute solutions, but it becomes increasingly and often forbiddingly complex in the case of real solids and liquids. Besides, the purely mechanical heat theory has its definite theoretical limitations. These become especially apparent when the thermal movements have become sufficiently intensive to affect the electric constituents of the atoms and molecules in a way to result in electromagnetic phenomena and the emission of electromagnetic waves. Heat as a form of energy is, of

course, subject to Planck's quantum restrictions. The modern theory of the specific heat of gases which takes the electromagnetic phenomena into account is due largely to Albert Einstein, while that for the specific heat of solids has been developed mainly by Debye. The greatest difficulties to theoretical treatment are offered by the liquids.

The intensity factor of thermal energy, the temperature, is empirically defined by the ideal gas law PV = RT and may be measured in any of the available thermometric scales. This definition involves the behavior of a material, though idealized, substance and hence is not of an absolute nature. An absolute scale that coincides with that derived from the ideal gas law was established by Lord Kelvin. From the impossibility of a "perpetuum mobile" of the second kind, he concluded that the maximal work that may be obtained from reversible movement of a certain amount of heat from a higher to a lower temperature must be the same irrespective of the substance involved. With an ideal gas as a work substance this maximal work is:

$$\Delta W = \frac{Q_1 \Delta T}{T_1} = \frac{Q_2 \Delta T}{T_2} \qquad 9.2$$

in which ΔW is the maximal work obtainable if the work substance withdraws an amount of heat energy Q_1 from a reservoir held at temperature T_1 and transmits an amount of heat energy Q_2 to a reservoir held at temperature T_2. With perfect reversibility, there is no entropy change; hence, $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$ and $\Delta W = Q_1 - Q_2$, or $\Delta W = \frac{Q}{T} \Delta T$. 9.2(a)

Since perpetual motion would be possible if another substance could give a maximal work different

from that obtainable by use of an ideal gas, the absolute temperature scale is thermodynamically defined by equation 9.2(a) and no longer by the ideal gas law. The scale unit employed in scientific thermometry is the centigrade. The scale starts at the absolute zero point; it reads 273.15°K for the freezing point and 373.15°K for the boiling point of water at a pressure of one atmosphere. The scientific capacity unit is the gram calorie per degree centigrade whereby the gram calorie is defined as the amount of heat required to increase the temperature of one gram of water from 14.5° to 15.5°C.

9.2 Heat Transmission

According to the Second Law of Thermodynamics, processes occur spontaneously if they result in an increase in entropy. Since the entropy of an amount of heat energy Q is Q/T_1 at the higher temperature T_1, and Q/T_2 at the lower temperature T_2 with $Q/T_1 < Q/T_2$, heat will move spontaneously from a location of higher to one of lower temperature. To achieve this end, heat, as any other energy, will employ all ways and means at its disposition. The mechanisms normally available for heat transmission are radiation, conduction and convection. Their relative importance in a particular case depends on the temperature level, the composition and structure of the system and on environmental factors. Thermal soil engineering problems may range from in situ burning of clay soils for foundation purposes to understanding and prevention of frost heave. This, combined with the fact that soils are normally composed of solid, liquid and gaseous phases, makes every aspect and mechanism of heat

transmission important to the soil engineer.

9.3 Radiation

Radiation is the predominant mechanism of thermal energy transmission from bodies at elevated temperatures through empty spaces or transparent media. Total radiation from a perfectly black body obeys the Stefan-Boltzmann law:

$$q = \sigma A T^4 \qquad 9.3$$

where q = rate of energy flow

A = area of the radiating surface

T = absolute temperature of the radiating body

σ = constant of black body radiation.

For imperfectly black bodies, σ is replaced by another factor. The commonly used value for σ is 4.96×10^{-8} in the c.g.s. system.

9.4 Conduction

The term conduction is reserved for the transport of heat through molecular momentum exchange between contiguous bodies or parts of a body in accordance with the kinetic theory. In gases, conduction is due to elastic impacts of molecules, in electrically non-conducting solids to longitudinal vibrations of the atoms or molecules, and in metals to such oscillations supplemented by movement of electrons. The basic law for heat conduction in one dimension is according to Biot and Fourier:

$$q = k \frac{A}{L} \Delta T \qquad 9.4$$

in which: q = energy flowing through area A per unit time when a temperature drop ΔT exists over a length L in the direction of the flow;

k = coefficient of thermal conductivity.

9.5 Convection

Heat convection is the transport and exchange of heat by mixing or interflow of multi-molecular masses of liquids and gases that are at different temperatures. It is controlled by the laws of fluid dynamics as well as by those of heat conduction.

9.6 Heat Transfer

Heat is propagated through space or different media in various manners depending on the type, composition and structure of the propagating substance. The only way that heat can be propagated through a vacuum is by radiation. Heat radiation emitted in accordance with the Stefan-Boltzmann law obeys the laws of geometrical optics and radiation physics including the restrictions of the quantum theory. Heat transport through gases and liquids may be by radiation, convection or conduction. In dense transparent solids, radiation may contribute to heat transport. However, the most important mechanism in solids at low temperatures is conduction. In porous or granular systems, convection of liquids and gases may contribute to heat transport. In dry soils at normal temperatures, most heat transmission occurs by means of conduction through their solid, liquid and gaseous phases. In moist soils, mass transportation

of the water substance contributes to the total thermal energy transport. Understanding of the behavior of a soil, a system composed of solid, liquid and gaseous phases, must be based on the knowledge available concerning the pertinent behavior of the separate phases and of their respective interphases.

9.7 Heat Conduction in Gases

The kinetic theory of gases provides a good foundation for the understanding and correlation of such properties of real gases as pressure, temperature, specific heat, internal friction, diffusion and heat transfer (9.8).

Viscous flow involves the transfer of momentum across a momentum gradient, thermal conductivity the transfer of kinetic energy across a kinetic energy gradient and diffusion the transportation of mass across a concentration gradient. The picture for thermal conduction in gases is that of molecules with higher kinetic energies moving to regions of lower kinetic energy, and vice versa, and exchanging energy by collisions. The basic relationships between the coefficient of thermal conductivity k and that of viscosity η is given by

$$k = \epsilon \, c_v \, \eta \qquad 9.5$$

in which ϵ = a factor with values between 2.5 and 1.0 and

c_v = mol heat of the gas at constant volume.

Table 9.1 presents data on dynamic viscosity and thermal conductivity for several gases at atmospheric pressure for temperatures of 0° and $100^{\circ}C$.

9.8 Heat Conduction in Liquids

In liquids the intermolecular attraction forces are sufficiently strong to lead to condensed systems, but not strong enough to prevent molecular translation and rotation. Thus, liquids fall between gases, with mutually independent molecules that move at random through space and collide with others only by chance, and solid crystals that hold atoms and molecules in nature's most orderly arrangement. Liquids have been treated theoretically as condensed gases and as degenerated crystals. A very profitable approach is to consider them as systems of contacting mobile molecules in which holes move at random. The relationship between holes and the liquid state is obvious from the fact that most solids expand on melting.

Heat conduction in liquids is, just as in gases, due to the kinetic energy of atoms and molecules. The actual mechanisms, however, are quite different. The most promising theory for liquids is that thermal energy is transferred from molecule to molecule by means of longitudinal vibrations similar to the propagation of sound. On this assumption, Bridgman (1923) derived an equation for the thermal conductivity of liquids. Because of its importance, this derivation is given in the following. If R is the universal gas constant and N the Avogadro number, then $3/2(R/N)\,\Delta T$ is the kinetic energy taken up by an atom of a monoatomic substance upon increase in temperature by ΔT.

Table 9.1

Coefficients of Dynamic Viscosity and Thermal Conductivity for Several Gases at 0° and 100°C and Atmospheric Pressure

Gas	Temperature 0°C		100°C	
	η 1)	k 2)	η	k
H_2	85	17.1	103	21.4
N_2	165	2.44	203	3.03
Air	171	2.44	218	3.08
O_2	193	2.44	247	3.13
CO_2	139	1.4	188	2.09

1) η = viscosity in micro poises
2) k = thermal conductivity in watt cm^{-1} $(°C)^{-1}$ x 10^{-4}

For relationships between different units of thermal conductivity, see Table 8.2.

Table 9.2

Equivalent Expressions of Thermal Conductivity

G. cal sec^{-1} cm^{-2} per °C per cm	Watts cm^{-2} per °C per cm	B.t.u. $hour^{-1}$ ft^{-2} per °F per inch
1	4.183	2903.0
0.2391	1.0	694.0
0.0003445	0.001440	1.0

The energy increase per atom or molecule in the solid state when heated by $1^{\circ}C$ is about $3R \times 1^{\circ}C$, one half of which is kinetic, the other half potential energy. Because the specific heat at constant volume Cv normally does not change much in the transition from the solid to the liquid state, the equipartition between potential and kinetic energy is considered as essentially true also for liquids.

For a temperature gradient dT/dx in a liquid with a molecular energy 3 RT/N, the energy difference between adjacent molecules in the direction of the temperature gradient is 3 RdTD/Ndx, where D is the mean distance between the centers of contacting molecules assuming simple cubic arrangement. If the difference in energy is handed down a row of molecules with the velocity of sound v, then the total energy that passes a fixed point of any row per unit time is.

$$\frac{3R}{N} \cdot \frac{dT}{dx} D \cdot \frac{v}{D} \cdot$$

Dividing this expression by the cross section D^2 , one obtains

$$\frac{3R}{N} \frac{dT}{dx} D^{-2} v.$$

By definition, the transfer per unit cross section under a temperature gradient $\frac{dT}{dx} = 1$ is the coefficient of thermal conductivity k.

Hence:

$$k = 3(R/N) v D^{-2} \qquad 9.6$$

Despite its simplicity, this equation yields data that are in good agreement with actual measurements including those on water whose thermal conductivity is about 2.5 to 5 times that of organic liquids.

The formula also gives the right sign for the temperature coefficient. But there are discrepancies between calculated and measured values for various liquids, especially glycerol.

Kardos (1934)[1] considered each molecule as a unit, possessing a definite amount of energy, and the drop in energy dQ and temperature dT restricted to the distance L between the surfaces of adjacent molecules. Multiplying by L/D the intermolecular energy drop over the distance L, the actual energy gradient is reduced to that of a quasi-homogeneous body. If heat is transmitted with the velocity of sound, then the heat flow per unit cross section is:

$$q = - Lv \left(\frac{1}{D^3} \; \frac{dQ}{dT} \; \frac{L}{D} \right) \left(\frac{dT}{dx} \right)_L .$$

From the basic equation of heat flow we have:

$$q = - k \left(\frac{dT}{dx} \right)_D = - k \, \frac{L}{D} \left(\frac{dT}{dx} \right)_L$$

in which the subscripts D and L denote the range over which the derivatives are taken. For cubical packing we obtain

$$\frac{1}{D^3} \cdot \frac{dQ}{dT} = \rho c_p$$

where ρ = density of liquid and c_p its specific heat at constant pressure. Hence, the coefficient of thermal conductivity k is given by:

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1) For a detailed review of this and other pertinent contributions peruse references (9.8) and (9.9) listed at the end of this chapter.

$$k = \zeta c_p v L. \qquad 9.7$$

Kardos gives a value of $L = 9.5 \times 10^{-9}$cm from consideration of the theory of Van der Waals forces, molecular weights, density and compressibility. For some liquids, the Kardos equation gives better values than Bridgman's, but it falls down in the case of glycerol. Table 9.3 presents data on the thermal conductivity coefficients of various liquids obtained by measurement and by calculation using the Bridgman and Kardos equations. There have been a number of more recent endeavors in this field. These include application of activation theory and consideration of hydrogen bonding, on the theoretical side, as well as a number of semi-empirical and empirical relationships for specific groups of liquids.

9.9 Heat Conduction in Solids

The ideal solid is the crystal. Between the solid and liquid states there exist a number of intermediate forms represented by rubbers, resins, glasses, liquid crystals and protoplasm. The outside symmetry of a crystal is an expression of the symmetry of its atomic or molecular building stones and that of their arrangement in space. The symmetry of a crystal evidences itself not only in the face development, but also in all other physical properties such as electric and thermal conductivity, density, elastic characteristics, piezoelectric behavior and refractive index. Only crystals of the highest symmetry have the same properties in all directions. Most minerals found in soils are of relatively low symmetry and their thermal conductivity can be expected to vary with direction within the crystal.

Table 9.3 (9.8)

Coefficients of Thermal Conductivity of Liquids from Experiment and Calculation According to Equations of Bridgman and Kardos, at 30°C

Liquid	v cm/sec x 10^{-3}	D cm x 10^{9}	k (watt/cm^2 per °C/cm)10^3 Bridgman	Kardos	Exper.
Water HOH	145	31.0	6.21		
	150	31.0	6.41	5.96	6.10
Methyl alcohol H_3COH	112	40.2	2.84		
	113	40.8	2.79	2.02	2.11
Ethyl alcohol H_5C_2OH	104	45.9	2.04		
	114	46.0	2.22	1.96	1.82
Isoamyl alcohol $H_{12}C_5OH$	124	56.5	1.60	2.21	1.48
Glycerine $H_5C_3(OH)_3$	191	49.5	3.20	5.75	2.81
Carbon bisulfide CS_2	96	46.0	1.87		
	106		2.06		
	118	46.6	2.23	1.47	1.59
Acetone $H_3C.CO.CH_3$	108	49.5	1.81		
	114	50.0	1.88	1.82	1.79
Ethyl ether $H_5C_2.O.C_2H_5$	92	55.0	1.25		
	92	55.9	1.21	1.40	1.37
Ethyl bromide H_5C_2Br	90	50.2	1.48	1.13	1.20
Ethyl iodide H_5C_2I	78	51.2	1.23	1.03	1.11

Note: Data for calculating coefficients were taken from (a) Chemical Engineer's Handbook, John H. Perry, McGraw-Hill (1943); (b) Handbook of Chemistry and Physics, Chemical Rubler Publishing Co. (1946). Values for speed of sound (v) were taken from Smithsonian Physical Tables; other values from Heat Transfer, M. Jakob, John Wiley and Sons (1949).

Theoretical treatment of heat transfer is based on the assumption that flow of energy between neighboring locations is proportional to the difference in internal energy. The heat flow q through a unit area in the x-direction can be written as:

$$q = - B \frac{du}{dx} = - B \frac{du}{dt} \cdot \frac{dT}{dx} = - Bc_v \frac{dT}{dx} \qquad 9.8$$

in which u = internal energy

c_v = specific heat at constant volume

B = constant

By definition: $q = - k \frac{dT}{dx}$, hence $k = Bc_v$. This leaves the problem of evaluating and understanding the physical meaning of constant B and property c_v. The most significant contributions in this area have been made by Debye (9.2). The theoretical treatment of the pertinent phenomena is quite involved and cannot be given here even in its barest outline. Also, even the best presently available theory cannot furnish dependable values for specific heats and thermal conductivity for soil systems as quickly and economically as well conducted experiments. It is desirable, however, to give pictures, crude as they may be, for the phenomena involved. Such pictures give meaning to experimental data, help one to judge whether or not they are reasonable and finally permit one to spot unexpected results that may be the starting point for

important practical as well as theoretical developments.

The crystalline structure may be visualized as atoms linked together by springs which transmit the thermal vibrations of the atoms from locations of higher to those of lower internal energy. This transmission is by two kinds of waves, compressional and distortional, that are propagated with different velocities. The wave energies themselves are subject to Planck's quantum laws. Many simultaneous wave trains exist which are unharmonic and therefore give rise to disturbances that increase with increasing temperature. This explains the decrease in thermal conductivity of crystalline solids with increasing temperature. The disturbances cause scattering of the thermal waves analogous to that of light waves in an opaque medium.

According to Debye, these thermoelastic waves are akin to acoustic waves. This permits the calculation of the coefficient of thermal conductivity k of pure crystalline solids by means of the equation:

$$k = 1/3\ c\ u\ \lambda \qquad \text{in which} \qquad 9.9$$

k = coefficient of thermal conductivity in cal/cm. $^{\circ}C$. sec

c = heat capacity of the lattice waves or phonons in cal/cm^3 . $^{\circ}C$. sec

u = velocity of sound in cm sec^{-1}, and

λ = mean free path of phonon, defined as that distance of travel which reduces its energy by scattering to 1/e of its original value; e is the base of the natural logarithms.

The mean free path of the phonons decreases with increasing temperature and at very low temperatures may be determined by the dimensions of the crystal itself (9.2).

If a solid body is composed of many crystals as in most actual crystalline substances, there will be a thin zone of disorder at the contact surfaces which affects thermal transmission even if the crystal system is of extreme purity. In the case of normal crystalline materials, impurities collect at the interfaces forming solutions that approach the properties of glasses. The latter have lower thermal conductivities than the corresponding crystals, but these conductivities increase with increasing temperature. Random orientation of crystals in multicrystalline bodies will average out directional differences in thermal conductivity within the single crystals.

When solid bodies are composed of different types of minerals with different conductivity behavior, the various mineral phases may be considered as arranged either parallel or in series, taking into consideration the effect of the interfacial contacts. In parallel arrangement, the conductivity of the system is the sum of the products of the partial volumes of the various minerals and their conductivities, while in series arrangement the resistivities, the reciprocals of the conductivities, are additive. Hence:

$$k_{(system)} = k_1 n_1 + k_2 n_2 + k_3 n_3 + \ldots\ldots\ldots - \Delta_k \quad \text{or} \qquad 9.10$$

$$r_{(system)} = r_1 n_1 + r_2 n_2 + r_3 n_3 + \ldots\ldots\ldots + \Delta_r \qquad 9.11$$

in which $r = 1/k$, k_i the conductivities and r_i the resistivities of the component mineral phases, while Δ_k , Δ_r are expressive of the effect of the area and type of interfacial contact zones. The results of these and related approaches have been reviewed in detail by van Rooyen and Winterkorn (9.8:9.9).

9.10 Thermal Conductivity and Resistivity of Soils

Soils are normally composed of solid, liquid and gaseous phases. The solid phases usually vary in size from pebbles to colloids and also in mineral character which may range from the relative simplicity of quartz, corundum and hematite to the complexity of the silico-aluminates that are representative of the clay minerals. The water and air phases may be continuous or discontinuous and may be present in various degrees of dispersion. The component phases are coupled in both parallel and series arrangement. Because of this complexity, needed engineering data must be based on experiment and correlation of experimental results into semi-empirical formulae, while theory serves as a qualitative though very important guide. From a theoretical and also from a practical point of view, there appear to be definite advantages in considering thermal transmission as a result of a driving potential and the resistance rather than the conductance of the system. For this reason, the concept of thermal resistivity is being used in soil engineering to an evergrowing extent.

The thermal resistivity of a system will be the smaller, the larger is the number of possible mechanisms of thermal transmission. In normal soil systems, such mechanisms include not only conduction in the interior of the various phases and transfer at the phase boundaries, but also micro convection in the gas phase and micro distillation and saltation of water molecules at water-air interfaces, similar to the jumping progression of sand grains due to wind action in the desert (9.1).

In moist soil, water transport is closely associated with heat transmission. Consequently, the thermal resistivity of moist soils can be smaller than the sum of the resistivities of its components, even under assumption of the most favorable, parallel, arrangement.

There exists a number of semi-empirical equations for calculating the thermal reisitivities of dry soils. As a good example, that of W. O. Smith is given below (9.7):

$$k = k_a P_a + k_o P_s \qquad 9.12$$

in which $k_o = \dfrac{1 + \alpha}{\dfrac{1}{k_s} + \left(\dfrac{1}{k_a} - \dfrac{1}{k_s}\right)\left(\dfrac{\alpha}{1 + \alpha}\right)}$

k_s = thermal conductivity of solids
k_a = thermal conductivity of air
P_a = total porosity

P_s = partial volume of solid framework

P_l = partial volume of material in the gaps between the grains

$\alpha = P_l / P_s$

The different types of soil structure considered by Smith are shown in Fig. 9.1.

9.11 Equations for Moist Soils

The more important equations developed for moist soils are those by Kersten and Makowski, the latter being based on Gemant's work (9.4;9.5).

Kersten's equations are as follows:

1. Silt and clay soils - water content 7% or more,

unfrozen: $k = \left[1.3 \text{ (log water content)} - 0.29\right] 10^{0.01 \gamma' - 3}$ 9.13

frozen: $k = 1.44 \times 10^{0.022 \gamma' - 5} + 12.2 \times 10^{0.03 \gamma' - 5} \text{(water content)}$ 9.14

2. Sandy Soils - water content 1% or more,

unfrozen: $k = \left[1.01 \log(\text{water content}) + 0.58\right] 10^{0.01 \gamma' - 3}$ 9.15

frozen: $k = 11.0 \times 10^{0.013 \gamma' - 5} + 4.6 \times 10^{0.01443 \gamma' - 5} \text{ (water content)}$ 9.16

where k is in watts/1°C cm, water content in percent of dry soil weight and γ' = dry density in lbs/ft^3.

Makowski's equation for non-frozen soil is:

$$k = \left[(1.424 - 0.00465\ p) \log_{10} m + (0.419 - 0.00313\ p)\right] \times 10^{d/100} \quad 9.17$$

where: k = thermal conductivity in watts/°C cm.

m = moisture content in percent of dry weight

p = percentage of clay in soil clay-sand mixture

d = dry density in lbs/ft^3

Nomograms of these equations are available. The results of the Kersten and Makowski-Gemant equations are in close agreement. Fig. 9.2 presents a nomogram prepared by Makowski and Mochlinski (loc. cit.) which also includes the solution of Kersten's equations for clay and sand.

9.12 Illustration of the Effect of Physical and Physico-chemical Factors on the Thermal Resistivity of Actual Soil Systems.

In the following, resistivities will be given mainly in thermal ohms (°C cm/watt) and conductivities in thermal watts/°C cm. Other

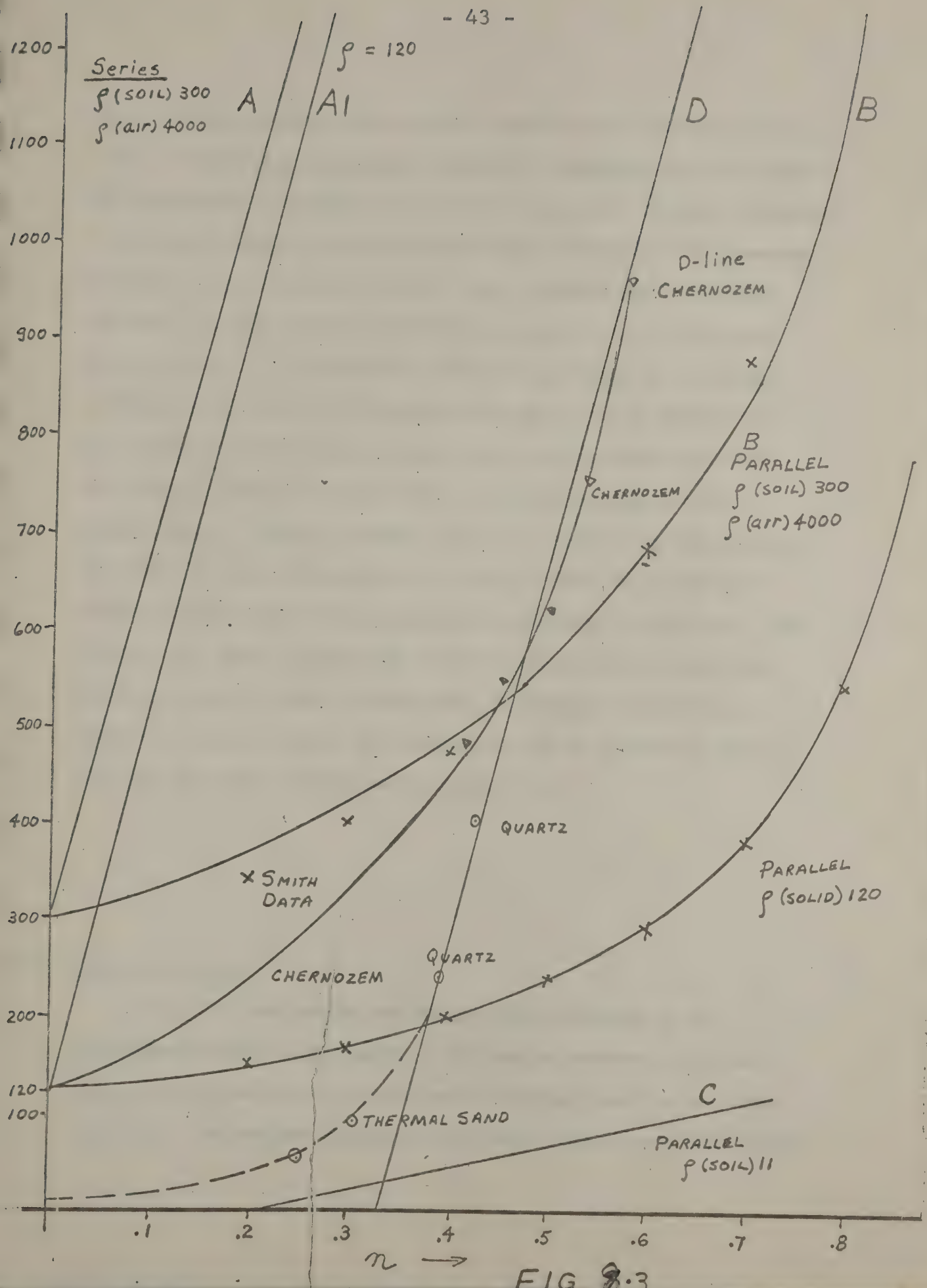

Series
ρ (soil) 300
ρ (air) 4000
A
A1
ρ = 120
D
B
D-line
CHERNOZEM
CHERNOZEM
B
PARALLEL
ρ (soil) 300
ρ (air) 4000
QUARTZ
SMITH
DATA
PARALLEL
ρ (solid) 120
QUARTZ
CHERNOZEM
C
THERMAL SAND
PARALLEL
ρ (soil) 11
1200
1100
1000
900
800
700
600
500
400
300
200
120
100
.1
.2
.3
.4
.5
.6
.7
.8
n →

FIG. 8.3

units are employed when they are more convenient for specific calculations. Table 9.4 gives average resistivity values for the more important constituents of common soils as well as for some related substances. Among these, quartz is by far the best heat conductor. The importance of atomic order or disorder within a solid constituent is shown by the fact that the thermal resistivity of quartz glass is ten times that of quartz ∥. No dependable data are available on the thermal resistivity of single clay crystals although it can be assumed that the blocky kaolinitic clays possess lower resistivities than montmorillonitic clays. One can obtain a probable minimum average resistivity for clays by assuming that it is similar to that for mica and that the ratio of the mica ∥ to mica ⊥ value is of the same order as that for the two corresponding directions in pine wood. This results in a mica ∥ value that is practically identical with that normally given for slate. Accordingly, an average resistivity of about 122 thermal ohms is the minimum that can be reasonably expected for clay minerals in random orientation (9.11).

9.13 Dry Soil Systems

In Fig. 9.3 are plotted experimental data obtained on dry American silt-clay soils (Smith), a dry Russian chernozem, several crushed quartz sands (van Rooyen) and two thermal sands at different densities. The thermal sands are well graded quartz sands that possess

Table 9.4

Average resistivity values in thermal ohms (rho)
for some soil constituents and allied materials

Material	Rho
Quartz ∥	7.9
Quartz ⊥	14.9
Quartz, random orientation	11.0
Quartz glass	79.0
Granite	26 - 58
Ca CO_3 ⊥	26.3
Marble	34 - 48
Limestone, dense	45
Ice	45
Sandstone	50
Dolomite	58
Slate	67
Water	165
Mica ⊥	170
Pine wood ∥	265
Pine wood ⊥	608
Organic material wet	400
" " dry	700
Air	4000

a small amount of kaolinite clay. The same figure contains theoretical curves for parallel and series arrangement of the solid phase, having thermal resistivities ρ = 300 and 120, respectively, and the air phase, with ρ = 4000. There is an additional curve for parallel arrangement of quartz (ρ = 11) and air, and a straight line D which crosses the B-line at n = 0.48 and runs parallel to the A-line.

It is interesting to note that at n $\approx$ 0.5 all dry, non-coherent soils possess approximately the same thermal resistivity and that all the experimental data fall between the B- and D-lines. Accordingly, from n = 0 to n $\sim$ 0.5 thermal transmission follows a mixed parallel and series arrangement whereby the influence of the latter increases with increasing porosity and becomes determinant at higher porosities. The greater the maximum potential density of the granular system and the greater the intrinsic conductivity of the solid constituents, the lower is the porosity at which the series arrangement becomes determinant.

The data obtained by Smith on American silt-clay soils indicate that for these the efficiency of thermal transmission through the contact interfaces is of the same order of magnitude as that within the individual crystallites. Of course, the total amount of contact areas decreases with increasing porosity. It seems that the oxygen molecules adsorbed on the dry mineral surfaces form a conductive bedding that possesses thermal transmission properties similar to those of the soil minerals. This is not surprising since volumetrically the most important component of soil minerals is oxygen which

represents 98.7 % of the volume of quartz and 87.2% of that of orthoclase.

If one calculates the mean free path λ of the phonons with the Debye equation $k = 1/3\ c\ u\ \lambda$ for quartz || and quartz glass, one obtains for the former a $\lambda = 4 \times 10^{-7}$ and for the glass a $\lambda = 4 \times 10^{-8}$ cm; the diameter of the oxygen atom is 2.64×10^{-8} cm. Hence, one would require a well ordered condensed oxygen film of only two atoms thickness to equal the mean free path in quartz glass which gives a resistivity of 70 thermal ohms.

9.14 Moist Soil Systems

The behavior of moist soil systems in thermal energy fields is of outstanding theoretical and practical importance. Fig. 9.4 shows data obtained by Kolyasev and Gupalo(9.10) on a chernozem soil from southern Russia at different densities and moisture contents. The original data were transformed into thermal ohms and were plotted against the fraction of the total porosity that was filled with water at the respective moisture contents and densities given by the authors. The actual volume occupied by the solid phase exerts a considerable influence on the thermal resistivity in both the very dry and the very wet states. However, the absolute volume of the solid phase plays only a secondary role when about 20% to 35% of the pore spaces are saturated with water.

9.15 Systems without Air Phase

Table 9.5 contains rho values for the chernozem soil at various absolute volumes of the solid phases extrapolated to 100% water saturation of the pore space. From these and the absolute volumes of both the mineral and water phases, the apparent resistivity of the mineral phase has been calculated under assumption of parallel and series arrangement, respectively, using a rho value of 165 for water. The data are given in columns 3 and 4 of Table 9.5. They show a regular decrease of the apparent rho (solid) with increasing absolute volume of solids yielding a lowest value for the series arrangement of 35.5 thermal ohms.

From our knowledge of the condition of water in cohesive soil systems, it is indicated to treat water-saturated soil systems as composed of three phases, i.e. mineral solids, solidified water comparable to ice, and free water. In addition, it appears that water molecules may become absorbed by the clay minerals and fitted in their crystal structure in solid solution. As a result of such solid solution, the thermal resistivity of clay minerals may decrease from an order of magnitude of 300 to about 100 thermal ohms. The thermal resistivity of water saturated clay systems is therefore not only a function of the respective absolute volumes of their components, their specific resistivities and their geometric arrangement, but depends also on the solid solution of water in the clay minerals and on structural changes akin to ice formation in the nominal liquid component. Much careful experimental work is needed before this

Table 9.5

Calculation of thermal resistivities of solid phase from extrapolated rho values of water saturated chernozem soil at different porosities (Kolyasev data) assuming parallel and series arrangement, respectively.

Porosity	rho values in thermal ohms		
	system	solid phase	
		parallel	Series
0.58	150	133	128
0.54	135	111	100
0.50	115	88	65
0.46	100	75	44
0.42	90	67	36

rho (water) = 165

very complex area can be scientifically organized.

9.16 Soil-Air-Water Systems

Fig. 9.4 shows that the absolute volume of the soil solids plays a relatively minor role with respect to the thermal resistivity of soils when from about 20% to 30% of the pore spaces are filled with water. This and other observations on thermal resistivity of soils as functions of moisture and air contents can be summarized and explained as follows:

1. In the absolutely dry state, increase in partial volume of solids increases the number and efficiency of contact areas between particles and decreases thermal resistivity of the system.
2. Small amounts of water are bound in solid solution within the clay minerals and decrease their intrinsic thermal resistivity.
3. Increasing moisture content up to about 10% by weight in the case of the chernozem soil is adsorbed around the areas of contact, thereby enlarging them and improving their effectiveness in thermal transmission.
4. From about 10% by weight, the water films around the soil particles form a continuous sheet over the internal soil surface. This water may be in three different states with different physical properties; two are represented by the surface zone vicinal to the air and solid phases, respectively, with the third lying inbetween. In this range, marked water movement

may occur in the film phase and also in the vapor phase by an evaporation condensation mechanism. These make an appreciable contribution to total heat transmission.

5. At about 20% of moisture, the importance of the film and airphase water transport decreases and heat conduction in the liquid or capillary phase enters the picture. As the moisture content increases above 25%, the rate of increase in overall thermal transmission slows down approaching the contribution from the intrinsic conductivity of water. As the latter replaces the air in the pores and reduces the area of existing air-water interphases, the effective thermal transmission mechanisms associated with such interphases is gradually replaced by the less effective one of thermal conduction in the liquid phase.
6. Finally, when about 60% of the available pore space is filled with water, the thermal resistivity remains constant with increasing moisture content. This occurs despite the fact that air with a resistivity of about 4000 thermal ohms is replaced by water with one of 165 thermal ohms.
7. The range in which the rate of decrease of thermal resistivity with increase in moisture content is greatest coincides with that in which considerable moisture movement takes place upon application of a thermal gradient.

9.17 The Problem of Moisture Movement under a Thermal Gradient

The thermal resistivity of soils at natural moisture contents is very closely related to the movement of moisture under thermal

gradients. A number of mechanisms have been proposed to account for such movement with particular emphasis on transportation in vapor or film phase, not excluding capillary and solid solution phenomena (9.10). An evaporation-condensation mechanism would be especially effective for heat transfer because of the large latent heat of evaporation possessed by water.

Table 9.6 presents experimental data on thermal moisture transmission coefficients for several clay- and soil-water systems at moisture contents corresponding to the respective plastic limits in the vicinity of which thermal moisture transfer is a maximum (9.3). Selecting a transmission coefficient of 3×10^{-6} cm^3/cm^2sec per $^oC/cm$ and a latent heat of evaporation of 580 cal/gram at 30^oC, the contribution to thermal transmission from an assumed evaporation-condensation mechanism can be calculated as follows:
$3 \times 10^{-6} \times 580 = 1.7 \times 10^{-3}$ cal/cm^2sec per $^oC.cm$. This corresponds to a contribution of 7.3×10^{-3} $watts/cm^2sec$ per $^oC/cm$.
A contribution of this order of magnitude to the thermal conductivity of a soil system can also be accounted for by assuming that the part of the water film that is proximal to the solid surfaces as well as the oriented water layer at the internal air-water interface are

in such condition or state that they possess thermal resistivity properties of the order of magnitude of normal ice.

In the face of the seeming equality in efficiency of heat transport by means of either an evaporation-condensation or an oriented film conduction mechanism, the question remains whether one mechanism alone could logically account for the level of actually observed resistivity values. Collection and analysis of a large number of experimental data produced the following findings:

Sand: of 919 rho values for sands of different densities and ranging in water content from zero to saturation, the average was 70.9 and the median 56°C - cm/watt. Fifty percent of the readings fell within the 33 and 77 band.

Clay: of 801 rho values determined on moist clays, the average was 54.9 and the median 54°C - cm/watt. Fifty percent of the readings fell within the 49 and 62 band.

Sandy Clay: of 329 rho values determined on sandy clays of various moisture contents, the average was 53.1 and the median 50°C - cm/watt (9.6).

Assuming the following reasonable thermal ohm values:

moist clay soil 55°C - cm/watt (at volume percent of: Solids = 50: water = 40; air = 10)

pure clay substance = 300

air = 4000

Table 9.6

Thermo-osmotic moisture transmission coefficients for H-Kaolinite, H-Montmorillonite and H-Grundite clays and for natural and several homoionic modifications of New Jersey Hagerstown soil in the moisture range of the plastic limit.(9.3).

Soil Material		Percent H_2O per dry weight of soil	Thermo-osmotic Tranmission coefficient $cc/cm^2 sec$ per $^oC/cm \times 10^6$
H. Kaolinite		30.6	3.4
H-Illite (Grundite)		23.5	1.6
H-Montmorillonite		61.8	1.9
natural	Hagerstown Soil	23.1	3.7
K		21.9	2.5
Mg		22.7	2.2
H		22.5	1.9
Cu		22.7	1.6
Al		23.1	1.5
Na		21.5	0.9

and straight additivity of the contributions to thermal conduction by the different phases, one obtains for the system:

$$k_{(system)} = \frac{1}{\zeta_{(system)}} = \frac{0.5}{300} + \frac{0.4}{165} + \frac{0.1}{4000}$$

$$= 0.0041 \text{ watt}/^{\circ}\text{C} - \text{cm or}$$

$$\zeta_{(system)} = 243^{\circ}\text{C} - \text{cm/watt (thermal ohms).}$$

Adding to this summation the previously calculated average value of 7.3×10^{-3} watt/°C - cm as a contribution from an evaporation-condensation mechanism, one obtains:

$$k_{(system)} = 0.0114 \text{ watt}/^{\circ}\text{C} - \text{cm or}$$

$$\zeta_{(system)} = 87.6\ ^{\circ}\text{C} - \text{cm/watt.}$$

Addition of an incremental contribution from an oriented film transfer mechanism, equal in amount to that from an evaporation-condensation mechanism, gives:

$$k_{(system)} = 0.0187 \text{ watt}/^{\circ}\text{C} - \text{cm or}$$

$$\zeta_{(system)} = 53.5^{\circ}\text{C} - \text{cm/watt.}$$

The last value compares well with the value of 54 previously given as the median of 801 rho values obtained on moist clays.

On the basis of the available evidence, it is safe to state that not just one, but several and possibly all rational mechanisms of heat and moisture conduction in soils that have so far been developed, contribute to the total observed phenomenon. The considerable difference in thermal conductivity reported for identical soil systems, located, respectively, above and below a heated plate, attests to the presence of an evaporation-condensation mechanism whose effectiveness is influenced by the lesser weight of the H_2O molecule as compared

with those of the N_2, O_2 and CO_2 molecules which are the normal constituents of the soil-air. The almost instantaneous establishment of a measurable electric field within a moist clay specimen upon application of a hot plate on one end and a cold plate on the other, long before the establishment of a thermal gradient within the sample, points to the existence of a structure of oriented water molecules that possesses sufficient rigidity to transmit the electric disturbance caused by the thermal shock and sufficient deformability to hold the impressed electric field. The described phenomenon is closely analogous to the hot-cold perception of the human skin and its transmission by means of the central nervous system.

II 6. INTRODUCTION TO SOIL STABILIZATION

13.1 DEFINITION

Soil stabilization is the collective term that covers any and all physical, chemical and biological methods employed to improve the properties of actual soils in order that they may serve satisfactorily for the intended engineering purpose. Different engineering uses pose different requirements regarding the resistance of stabilized soils to physical, physico-chemical and chemical forces; included in this is resistance to weathering and microbial decomposition of soil and stabilizer components. To stabilize a soil so that it will successfully carry a heavy bomber is vastly different from stabilizing the slope of a cut or fill against erosion.

The term soil stabilization, therefore, possesses a definite meaning only if properly specified. Within the domain of soil stabilization are such diverse items as slope protection against erosion; improvement of strength and volume stability of sandy foundation soils by vibratory densification; impermeabilization of loose porous and fissured rock by means of clay, cement and chemical injections; compaction of earth dams; impermeabilization of the bottoms of lakes and ponds by increasing the swelling capacity of their clay fractions with Na-ion treatment; and many others. The largest and most important use of soil stabilization so far has been in providing bases and occasionally surfaces for all types of roads, landing places and similar facilities. In this use, the stabilized soils are subjected not only to the static and dynamic, single and repeated loadings incidental to their engineering function, but also to the warming-cooling and wetting-drying cycles of the local microclimate. This means that the

problem of weather resistance and durability in general looms large and must be dealt with in soil stabilization.

The best engineering solutions of the various problems of soil stabilization are based on:

(a) knowledge of the mechanical properties of the soil under consideration, obtained by actual measurement with recognized and dependable methods. This requires at least a qualitative understanding of how the measured properties depend on the granulometry of the soil, on the mineralogical and (or) chemical character especially of the smallest size components, on general surface physical and chemical characteristics and on the structural arrangement of the soil constituents;

(b) knowledge of the intensity and type of mechanical and weathering forces to which the stabilized soil system will be exposed in its engineering service and of the expected interaction of the soil system with these forces;

(c) a genuine, even if only qualitative, understanding of physics and chemistry especially as related to surface and colloidal phenomena. This will enable the engineer to select the proper treatment after diagnosis has been made on the basis of the items named in the preceding paragraphs.

One who desires to stabilize a soil finds himself in much the same situation as a practicing physician. There exist striking analogies between the sources they have to draw on, the creative imagination by which piecemeal data are built into working concepts, and their integration by practical experience. (13.5)

13.2 Main Fields of Application of Soil Stabilization

Soil stabilization undertaken to produce traffic and weather resistant bases and surfaces is of primary usefulness in the following situations:

(a) when a country or region must be lifted out of the sand or mud in order to have access to markets for its own products and to allow low cost transportation for imports necessary to its life and economic development;

(b) when a good primary road system is available but adequate secondary and feeder roads are lacking;

(c)when, in order to meet external competition that might threaten the very existence of an indigenous agriculture, the latter must be rationalized into units of optimal productivity, which requires the construction of a corresponding appropriate net of traffic ways;

(d) when in the building of highest type interstate and interregional roads, granular materials such as gravels and crushed stone are either not available or are of insufficient quality to serve as base construction material;

(e) when in providing road and street facilities for suburban developments one wants to take advantage not only of the inherent economy of soil stabilization, but also of the sound absorbing or acustic advantages of certain stabilized soil systems;

(f) when military or other emergencies make land locomotion necessary over soils that without stabilization would not permit such locomotion.

In the engineering use of soil stabilization, one must first assay the mechanical and physico-chemical properties of the given soil and clearly define the amount of improvement or stabilization required for the intended

use. This must be expressed in physical or physico-chemical terms. These scientific terms must then be translated into available materials and practical procedures. At this point also a decision must be made whether time or money economy is the deciding factor in the choice of material and method. In times of war or other crisis, a job may have to be done as quickly as possible regardless of cost.

The execution of soil stabilization involves essentially three unit processes: (a) comminution, loosening or uniformizing of the soil, (b) mixing with the stabilizing material, (c) densification and finishing. The efficiency of each of these processes depends on the type and condition of the soil employed and on the machines or implements used. While the physics and economics of each of these steps has been well investigated, they still represent fertile fields for scientific and engineering inquiry.

Pertinent economic considerations cover the cost of materials including that of their transport, the cost of processing to the finished product, the useful life of the system and the cost of maintenance during the useful life. Sometimes, the use of special activating substances not only improves the final product and increases its service life, but also reduces mixing and compacting costs sufficiently to counterbalance the cost of the additive or even to result in an actual lowering of total construction costs.

13.3 Soil Classifications and Soil Stabilization

For stabilization purposes, soils are subdivided into two large groups depending on whether or not they possess a granular (sand or sand-gravel) skeleton in the densified state in which they are used. This coincides with the AASHO classification in which the two groups are called (a) granular and (b) silt-clay materials, respectively. Among

the latter fall the soils that possess more than 35% of material passing the No. 200 sieve. This, of course, is a general dividing line valid for average natural North American soil materials. Physically, one may express the maximum amount of silt-clay material permissible in a granular soil as that which combined with its moisture content at the plastic limit just fills the pore space between the grains of the densified granular bearing skeleton without intervening between the points of contact of these grains. Since the porosity of the granular system without the silt-clay material is a function of its granulometry, the limit of 35% of silt-clay material is a general one holding good for average granulometry of the sand-gravel components and average water affinity of the silt-clay materials. Adjustments have to be made for deviations from the average or normal.

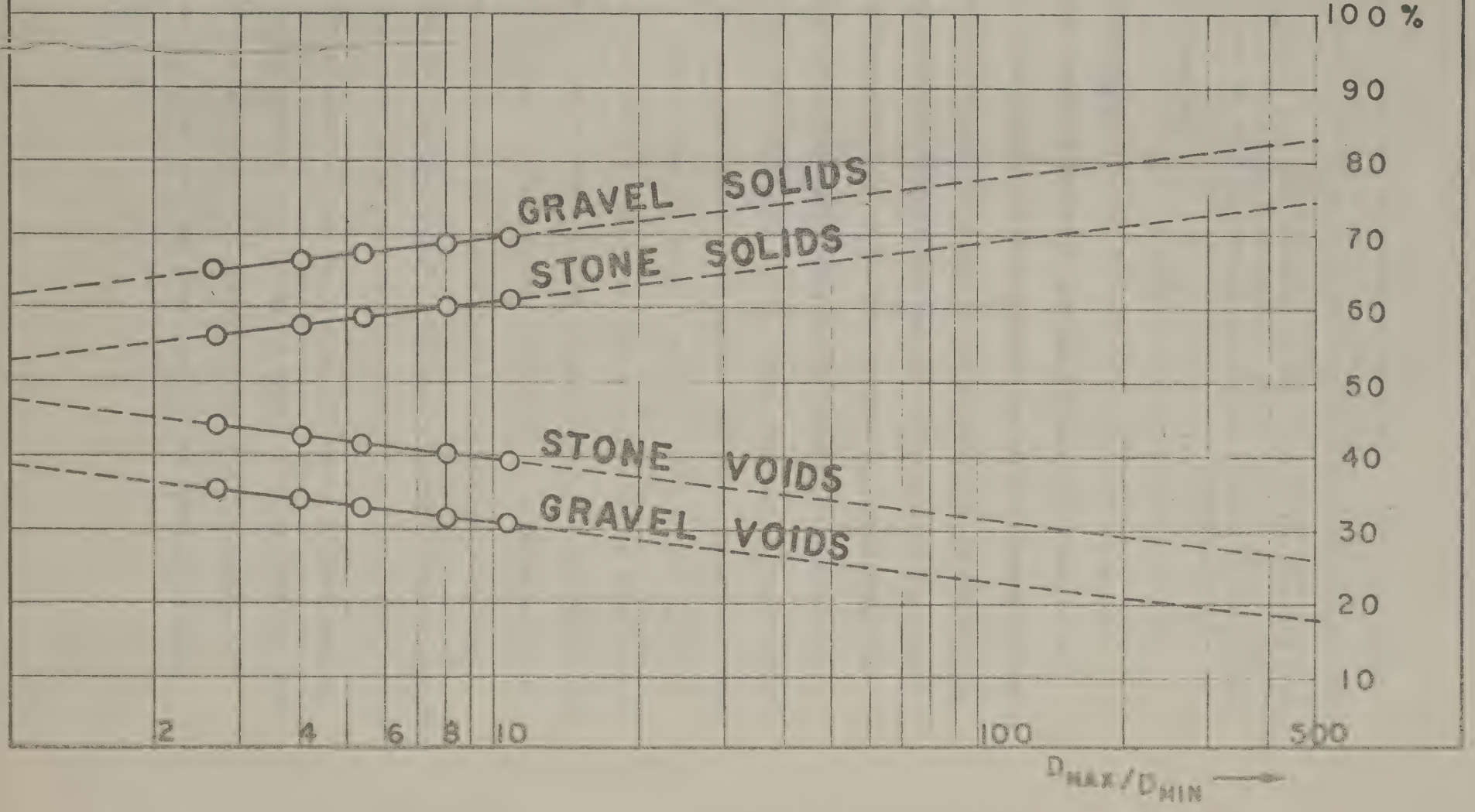
13.4 Granular Materials.

The principles of packing of granular particles of equal and different sizes have been discussed in Chapters 4 and 5. In the case of continuous grading of the particles, the degree of packing or the porosity of a granular system that can be obtained with moderate packing effort is a function of the size range of the particles. This is well known not only in soil, but also in concrete technology.

Fig. 13.1 gives the relationship between porosity as obtained by standard rodding of mineral aggregate and the size range of the latter as expressed by the ratio of maximum to minimum diameter. These relationships have been obtained by extrapolation from practical design data involving coarse aggregate of various size ranges. (13.2) Since these relationships are essentially of a geometric nature, they do not depend on actual particle sizes. The data from which the relationships given in Fig. 13-1 are

—FIG. 13.1

RELATION BETWEEN NORMAL POROSITY AND SIZE RANGE AS EXPRESSED BY D_{MAX}/D_{MIN} IN CONTINUOUS GRADING.



derived represent a large body of empirical knowledge. Their scientific significance, however, is evidenced by the fact that with identically sized grains, i.e. $D_{max}/D_{min} = 1$, the porosity in the case of the rounded gravel corresponds with that of rhombic packing and in the case of crushed stone with that of cubic packing.

13.5 Silt-Clay Materials.

Accepting the amount of material passing the No. 200 sieve as a scientifically and practically justified indicator of the general character of a soil, it would be logical to assay the water affinity of the soil by tests on the -200 sieve fraction itself and not indirectly on the fraction passing the No. 40 sieve. The common tests for the liquid and plastic limits made on the latter are influenced by the amount and granulometry of the fine sand fraction contained in it. Some progressive organizations are already making the consistency tests on the -200 sieve fraction without or in addition to tests on the -40 sieve fraction. Only on the basis of tests made on the -200 sieve fraction can the actual dividing line between granular soils and silt-clay materials be established for a particular soil combination. With respect to the ease or difficulty of stabilizing a silt-clay material, we have as valuable indicators (a) percentage and water affinity of the material passing the No. 200 sieve as shown by sieve analysis and consistency tests made on either the -40 sieve or the -200 sieve material; (b) the ratio of material passing the No. 200 sieve to that passing the No. 40 sieve (dust ratio); (c) the group index value and (d) the pedologic character of the material with regard to any or all categories of the pedologic classification that are pertinent to the specific problem under consideration.

13.6 Stabilization of Soils Possessing a Granular Bearing Skeleton

Soils possessing a granular bearing skeleton in well densified condition may have silt-clay contents from zero to about 35% and varying water affinity and cementing power of its silt-clay fraction. The term silt-clay materials denotes not only a particle size range, but also particles of predominantly aluminosilicate composition that have been normally weathered in the presence of water and possess cohesive properties. If because of composition or the absence of water, such particles possess no cohesive properties, then they must be considered as fine-granular materials that follow the same packing laws as coarse granular (sand and gravel) materials. This is especially pertinent in the stabilization of fine grained lunar surface material. The more of the space between the coarser components is filled with silt-clay material, the smaller is the permeability of the system and the greater normally its cohesive strength in semi-dry condition. Soils without a silt-clay fraction possess no cohesive strength and their mechanical resistance is a function of the coefficient of internal friction (tan φ) times the forces normal to the shear plane and of the degree of interlocking of the coarse particles. The latter is especially important in the case of irregularly shaped crushed stone particles and is made use of in crushed stone bases, especially those of macadam type. Natural sand and gravel aggregate usually tends to be rounded; interlocking loses its importance with increasing degree of sphericity and with increasing size range, especially in the case of continuous gradation. Hence, for most natural non-cohesive granular materials, the shear resistance can be written as:

$S = N \cdot \tan \varphi$, in which

S = shear resistance per unit area of shear plane

N = compressive stress normal to the shear plane

$\tan \varphi$ = coefficient of internal friction.

Accordingly, the mechanical resistance of granular materials is very low in the surface layers where the normal pressure on the shear planes is small and derives only from the weight of the overlying granules. Such systems require cementation for stabilization to dependable strength properties. Cementation also prevents segregation of the granular particles that possess different sizes.

13.7 Cementation Stabilization of Granular Soils

Cementation stabilization of granular soils makes them members of a large group of engineering materials that have been called collameritic (colla = glue or cement; meros = particle) systems. Some other representatives are listed below:

Material	Particles	Cementing Agent
Portland Cement Concrete	Gravel and Sand	Portland Cement
Sandstone	Sand	Mineral cementing material
Mortar	Sand	Lime or cement paste
Wood	Cellulose Fibers	Lignin

The properties of collameritic systems depend on

(a) the granulometry (sizes, shapes, gradation, packing characteristics) and the mechanical strength and durability of the particulate components;

(b) the mechanical strength, weathering and chemical resistance of the cementing material; and

(c) the interaction between the cementing material and the surfaces of the mineral particles determining the strength of bond between them.

The mechanical strength of such systems depends on the weakest link which is only rarely the strength of the particles and usually that of the cementing material. In the case of a well graded system such as one of rounded gravel and sand corresponding to the Fuller curve, the mechanical strength of the system depends mainly on the strength of the cement and on the proportion of the pore space occupied by it. (13.1) This relationship was expressed by Feret in the following form:

$$S = k\left(\frac{c}{1 - s}\right)^n$$

in which S = compressive strength

k = essentially the strength of the cement but influenced by particle strength, granulometry and packing,

c = absolute volume of the cement per unit volume

s = absolute volume of particles per unit volume

n = constant depending on material and geometric factors.

This equation shows that (a) the volume of cement required to produce a predetermined strength increases with increase of the porosity of the particulate system and (b) the strength that can be obtained with a certain amount of cement rises exponentially with increasing ratio of the absolute volume of the cement to that of the porosity. While originally developed for lime and hydraulic mortars, the Feret formula has proved itself essentially correct in as widely differing collameritic systems as portland cement concrete and beach sands, stabilized by means of synthetic resins.(138)

In granular systems that possess a significant amount of internal surface, the adsorption capacity of the latter must be satisfied by an incremental amount of cement added over that calculated by means of Feret's equation.

13.8 Cementing Materials.

For the cementing stabilization of granular soils, a great variety of both inorganic and organic cementing materials can be employed. Most economical is normally the use of natural silt-clay materials. The resulting systems can be called clay-concretes or clay mortars, respectively; under such names as mechanically or granular stabilized soils and sand-clay these systems are among the oldest representatives of soil stabilization. Typical specifications for clay concretes and clay mortars are given in Table 13-1. Fig. 13-2 presents a granulometric soil chart in which the areas I, II and III indicate the relationship between granulometric composition and suitability of stabilized mixture for various engineering requirements.

Clays and silt-clay materials possess several disadvantages as cementing agents, the most important of which are their water affinity and capillarity which result in change of their moisture content and consistency with every change in temperature and moisture condition of the environment. For this reason, methods have been developed to control their water affinity by means of water repellant materials, such as bitumen or natural, modified and synthetic resins, or to replace the clay binder partly or completely by means of stronger and water resistant inorganic or organic cements. If complete replacement is made with portland cement, then the respective portland cement concrete or mortar is formed. There exists, then a complete

Table 13.1

Gradation Requirements for Soil-Aggregate Materials
(A.S.T.M. Specs. D 1241-55 T)

Sieve Size (Square openings)	Percentage by Weight Passing Square Mesh Sieves					
	Type I				Type II	
	Gradation A	Gradation B	Gradation C	Gradation D	Gradation E	Gradation F
2 in.	100	100				
1 in.		75 to 95	100	100	100	100
3/8 in.	30 to 65	40 to 75	50 to 85	60 to 100		
No.4 (4760 micron)	25 to 55	30 to 60	35 to 65	50 to 85	55 to 100	70 to 100
No.10 (2000 micron)	15 to 40	20 to 45	25 to 50	40 to 70	40 to 100	55 to 100
No.40 (420 micron)	8 to 20	15 to 30	15 to 30	25 to 45	20 to 50	30 to 70
No.200 (74 micron)	2 to 8	5 to 20	5 to 15	10 to 25	6 to 20	8 to 25

series of compositions with corresponding engineering properties that range from a clay concrete to a portland cement concrete. This is illustrated by the data in Table 13-2; the same type of series exists for any and all other cementing materials. Fig. 13-3 gives a grading band for waterprcofed granular soil stabilization which involves the use of from 1% to 2% of liquid asphalt based on the weight of the mineral particles.

13.9 Interrelations between the Granulometry of the Particles to be Cemented and That of the Cementing Material.

Furnas (loc. cit. Chapter 5) has shown that adding of smaller sized particles to systems of larger sized ones, in amounts smaller than necessary to occupy the pore space, will nevertheless decrease the packing density of the larger particles. This interference will be minimal and practically zero if the size ratio of the particles is 100 or more to 1. This must be kept in mind in the choice of a cementing agent for non-cohesive granular materials, especially if the latter are of small size such as for example assumed to exist on the lunar surface. If such a dust had an effective particle size of 10^{-5} cm, then that of the cementing material at the time of densification should not be larger than 10^{-7} cm if marked interference with the packing of the larger particles is to be avoided.

Portland cement ground to a surface area of 1700 cm^2 per gram and 5355 cm^2/cm^3 would have an average particle size of 1.8×10^{-3} cm and its particles could be expected to show measurable interference with the packing of sand grains smaller than 2 mm, or passing the No. 10 sieve. For this reason, the best sands for making portland cement concretes are rather coarse. Another way of looking at this problem is to compare the

Table 13.2
Summary of Test Results on Various Concretes

Batch No:	1	2	3	4	5	6	7	8
Cement Used:	clay	3/4clay 1/4P.C.	1/2clay 1/2 P.C.	1/4 clay 3/4 P.C.	All P.C.	1/2 clay 1/2 A.F.	1/2 clay 1/2sorel	1/2 clay 1/2 2 M.C.2
p.c.f. Weight of								
Aggregate	119	119	119	119	119	119	119	119
Clay	29.1	21.8	14.6	7.3		14.6	14.6	14.6
Water	5.8	6.9	8.0	9.1	10.2	2.9	5.0*	2.9
Portland Cement		5.0	10.1	15.3	20.3			
Aniline						7.1		
Furfural						3.6		
MgO							10.1	
$MgCl_2$							9.5	
M.C. 2								8.2
Voidless Density	153.9	152.7	151.7	150.7	149.5	147.2	153.2	144.7
Actual Densities of Cylinders p.c.f.	141 145 139	145 136 145	148 149 147	151 152 150	147 148 150	141 142 142	144 144 144	133 132 133
Compressive Strength at 46 days p.s.i.	83 # 65 #	619 170	1710 2200	4050 4220	4380 3870		422	7 8
Compressive Strength at 130 days		1112	2810	4920**	5425	1780 1060 830	725 741	

* Added for workability ** Segregation at one end # Tested dry

effective surface area of the particles to be cemented with that of the cement dispersed into the effective particle size actually occurring during mixing and densification. Should the soil particle sizes be in the order of 10^{-6} cm, then the size of the cementing particles should be of the order of 10^{-8} cm or of molecular size.

The practical application of the basic principles of cementation stabilization is well demonstrated in the development of methods for the stabilization of military beach heads as well as in the engineering considerations concerning possibly necessary stabilization treatment of lunar surface materials. (13.8)

13.10 The Stabilization of Silt-Clay Materials.

The shear resistance of silt-clay soils is normally expressed by the equation:

$$S = N \tan \varphi + C$$

in which S = shear resistance per unit cross section

N = normal stress on the shear plane

$\tan \varphi$ = coefficient of internal friction

C = cohesion per unit cross section

As discussed in Chapter 11, this equation is only a crude approximation. Actually, friction and cohesion are not independent of each other and both depend on the degree of packing, moisture content, granulometry and secondary structure of the solid soil constituents, and on the previous history of the soil system. The frictional part of the shear resistance can be expected to follow the previously indicated volume law: $\tan \varphi = \frac{k}{V - V_s}$ while the cohesion or bonding strength can be expressed formalistically

as:

$$C = I \tan \varphi_c \text{ in which}$$

I = internal pressure or attraction forces acting across shear planes

$\tan \varphi_c$ = coefficient of friction which when multiplied with I gives the experimentally determined value of C.

The cohesion of a silt-clay soil is due to its water content, i.e. the mutual attraction and bonding of the water molecules. The closer these molecules are to the particle surfaces, the less is their freedom of movement and the more effective are their mutual bonding forces; the farther away these molecules are from the surface, the more they behave as in normal water. For the most effective mutual arrangement of two water dipoles, we have a bonding energy per mole of 4.84 k cal and a bond length of about 2.37 Å. From these data and the dimensions of the H_2O molecule, the individual bond strength can be calculated to be of the order of 10^4 kg/cm^2. The internal pressure I of liquids can also be calculated from the equation

$$I = \frac{2\sigma}{x}$$

where σ is the surface energy in erg/cm^2 which is numerically equal to the surface tension and x is the bond length in cm. Using σ for water at 18°C = 72.8 erg cm^{-2} and x = 2.37 x 10^{-8} cm, we obtain

$$I = 145.6/2.37 \times 10^{-8} \text{ erg/cm}^2 = 6100 \text{ kg/cm}^2.$$

Even with small coefficients of friction, internal pressures of this magnitude may make a considerable contribution to the shear resistance of soils. This contribution will be the larger the greater is the restraint or fixation of the water molecules concerned by vicinal particle surfaces, i.e. the lower the moisture content of the system.

Accordingly, silt-clay soils may possess at low moisture contents sufficient mechanical resistance properties to carry even very high traffic

loads. However, as soon as such soils are exposed to contact with free water, this is taken in as a result of their water affinity and capillarity, whereby the thickness of the water films that join the particles is increased and the shear resistance of the system decreased. The water films change from cementing to lubricating agents. With increasing water content, the system changes from what was essentially a solid to a state of secondary plasticity and finally that of a liquid, with viscous or creep properties in evidence already in the plastic state. Liquifaction is hastened by traffic that squeezes free pore water between the particles and tends to homogenize the system, making the interparticle water wedges thicker than would have resulted from free satisfaction of the water affinity of the particles alone. The heart of the problem of stabilizing cohesive soils is that the troublesome water affinity of the soil minerals is also the cause of the very desirable cohesive strength at low moisture contents of the soil system.

A basic consideration in the stabilization of cohesive soils without granular bearing skeleton derives from the following important fact. Even though such soils may, with the use of proper dispersing agents and plenty of mechanical energy, be subdivided into their individual particulate components, in actual practice one deals with secondary aggregations of the individual particles into crumbs that are normally several millimeters in size. It is these secondary particles that are treated and forged into a stabilized system. For such stabilizing treatment, the soil crumbs should have a moisture content high enough to leave little or no residual affinity for water and low enough to keep the crumb from being markedly plastic. The moisture content range concerned is also that of optimum tilth at which

the soil can be brought to the desired crumb size at lowest expense of mechanical energy. For the stabilization itself, there are three basic possibilities:

1. Cementation of the secondary particle aggregations by means of inorganic bonding agents that are resistant to the action of water;
2. Waterproofing and bonding of the secondary aggregates by means of water repellent organic cements;
3. Maintenance of a portion of the natural water affinity and cohesion properties of the soil and especially clay particles and waterproofing by means of organic materials to protect the system against excessive water intake and concomitant lowering of its shear resistance.

Actual processes usually involve at least two of these possibilities.

13.11 Cementation by Means of Inorganic Binders.

Most inorganic cementing agents such as portland cement, hydrated lime, the various gypsum plasters, Sorel cements and others possess particle sizes that exceed those of the primary clay particles. Hence, even if one could afford the work to separate a soil into its primary components, the material required to surround each particle with the cementing agent would exceed in volume that of the solid components of the soil to be stabilized. For this reason and those mentioned above, the actual stabilization mechanism with inorganic cements consists of:

(a) stabilization of the natural or artifically produced secondary aggregations or crumbs by a surrounding layer of cementing substance which forms a hard water resistant case that also infests or grows into the porous crumb, and

(b) subsequent bonding together of the "case hardened" crumbs by the outermost layers of cementing material which may or may not become somewhat diluted in the mixing and compaction process by some finely subdivided soil material.

It is logical that achievement of satisfactory stabilization requires lesser amounts of cementing substances with increasing intrinsic water resistance of the natural or artifically produced soil crumbs. As shown in Chapter 3, the water resistance of secondary soil aggregations depends on physico-chemical soil factors which usually influence the stabilization of cohesive soils in both a direct and indirect manner, the indirect one acting through its effect on the development and water resistance of secondary soil aggregations. These influences have been thoroughly investigated for stabilization of clay soils with portland cement. (13.4) The main results of these investigations may be summarized as follows:

1. Successful stabilization of clay soils by means of portland cement depends not only on physical, but also on physico-chemical factors;
2. Stabilization is facilitated by certain types of exchange ions and rendered more difficult by others;
3. The difference between the shrinkage limit and the optimum moisture content of normal Proctor compaction is an indication of the ease or difficulty of stabilizing a particular soil. The higher the shrinkage limit, the greater is normally the water resistance of the soil crumbs and the less cement is required for their stabilization.
4. The resistance of a soil-cement system against the deteriorating effect of wetting and drying cycles decreases with increasing water affinity and accessibility of its internal surface.

5. The resistance of a soil-cement system against the deteriorating effect of freezing-thawing cycles depends upon the permeability of the system and especially on the pore space filled with free water that freezes under expansion as against the water bound by the mineral surfaces and exchange ions.

6. Increasing the degree of compaction at constant moisture content decreases the distance between the particles and increases the bond strength as well as the coefficient of internal friction; by decreasing the porosity, it decreases the accessibility of the internal surface and the pore space portion available for free water which freezes under expansion. Hence, increase in dry density increases strength and weathering resistance of soil-cement as long as sufficient water is available to satisfy the hydration needs of the cement and of the soil mineral surfaces.

7. Increasing the moisture content at constant dry density has in general a favorable effect except for soils of very low water affinity. The reason for the favorable effect is the more complete original satisfaction of the water affinity of the soil and cement particles. This phenomenon is also important with respect to the strength properties of cohesive soils compacted without portland cement.

8. The presence of appreciable quantities of soil organic matter is in general undesirable. Its specific detrimental effect depends on the type of organic matter and thus on the genetic soil class.

9. The quality of soil-cement systems is adequately determined by the standardized wetting-drying and freezing-thawing tests. The freezing-thawing cycles are recommended, even for use in regions in which soil

freezing does not occur, for soils that possess a certain resistance to wetting, as do some chernozems. In such soils, the freeze-thaw cycles help to "pump" moisture into the system which also occurs under normal temperature fluctuations above freezing temperature, though requiring much longer time periods.

10. Since the standardized weathering cycle testing requires about 4 weeks time, it is desirable to correlate it with simpler tests requiring less time, such as determination of compressive strength of specimens after a curing period of a few days. Such secondary standards are already in wide use. It is important, however, for regions and soils for which specific stabilization experience is not yet available to use the simpler secondary tests only after establishment of their correlation with the standard weathering tests.

11. When emergency situations prohibit performance of primary or secondary tests previous to actual construction, decisions can be made on the basis of past experience under proper consideration of the granulometry, consistency properties, shrinkage limit and optimum moisture content of the soil involved.

Excellent literature on the various types of cementation stabilization is available from the Portland Cement Association, the National Lime Association, the Highway Research Board, and other agencies.

13.12 Stabilization with Organic Cements and Waterproofing Agents.

Cementation stabilization with organic binders.

The purpose of pertinent processes is to deprive primary and secondary soil particles of their water affinity and to bind them together by means of a strong organic cement. These two functions may be achieved by one and

the same agent or by means of two or more substances which are applied either simultaneously or in a predetermined optimal sequence. The ideal binder is water repellent, has a greater affinity than water for the particle surfaces, resists attack by bacteria and fungi, and is applicable as a liquid or mixture of liquids of relatively low viscosity which subsequently polymerizes to form a strong solid or plastic binder. Substances that fulfill all these conditions are available but their costs are too high for normal construction purposes. They are, however, valuable for emergencies.

13.13 Waterproofing Treatments of Cohesive Soils

From both a theoretical and practical point of view, the most attractive solution of stabilizing a cohesive soil is to preserve as much as possible of the cohesion causing water affinity, but to reduce the latter sufficiently to prevent intake of undesirable incremental water. This can be done on a macro-scale by completely enveloping with a bituminous membrane a whole soil layer compacted at optimum water content to maximum density. It can also be done on a micro-scale by protecting in an analogous manner moist soil crumbs and forging them into a system in which the individual coated crumbs are bound together with a water repellant bituminous cement.

13.14. Practical Mixed Systems

While theoretically a differentiation may be made between the systems defined above, the practically important systems are usually of a mixed character. The indicated extreme types and all intermediate members can be obtained in bituminous stabilization of cohesive soils by variation of procedures or by the supplemental use of chemically active additives. In

the contemplated use of bituminous stabilization for cohesive soils without granular bearing skeleton, the following potential deficiencies of the bitumen must be kept in mind:

(a) Inability of the bitumen to destroy the water affinity of the soil constituents or to protect the secondary aggregations from water intake using bitumen film thicknesses that are small enough that the system will not have too high a bitumen content which would result in lowering of the mechanical strength of the system at high summer temperatures.

(b) Possibility of chemical change of the bituminous materials in their use as thin films through oxydation and attack by soil bacteria and fungi. Such deterioration can be prevented by use of antioxidant and bacteri- and fungicidal additives to the bitumen.

The problem of the adhesion of bitumen on mineral surfaces as compared to the affinity of water for the same surfaces has received extensive study and several methods have been developed for improving the mineral-bitumen bond and decreasing the danger of stripping off the bitumen by preferential adsorption of water. These methods attempt either

1. to change the chemical character of the surfaces of the mineral particles,; or
2. to increase the affinity of the bituminous materials for normally hydrophilic minerals by admixture of small amounts of surface active substances which ideally form insoluble water repellant compounds with chemical constituent of the mineral surfaces; or
3. to change both the mineral surfaces and the composition of the bituminous materials.

As examples for the effectiveness of changing the surface-chemical properties of the soil and especially clay minerals may serve the results of an eight-year research project undertaken in the Thirties by the Missouri State Highway Department. (13.3) This research was concerned with the susceptibility to bituminous stabilization of six pedologically different clay soils with their natural exchange ions as well as after change into eight different monoionic (Na, K, Mg, Ca, Ba, H, Al and Fe) modifications. Each soil modification was tested with asphaltic cutbacks from twenty-one different crudes, three normal coking tars (RT-2; RT-4, RT-5) and two low temperature tars. All in all, 1404 different combinations were tested. Rigorously condensed, the results can be stated as follows:

1. Influence of the Clay Mineral Composition

The larger the ratio of $SiO_2/Al_2O_3 + Fe_2O_0$ in the clay mineral fraction and consequently the base exchange capacity and water affinity, the greater the difficulty of bituminous stabilization.

2. Influence of the Exchange Cations

The higher the valency of the exchange ions, the easier was the stabilization of the soils. Na-soils, irrespective of the type of clay mineral, could not be stabilized, while all Al- and Fe- soils gave excellent results even if the respective soils could not be stabilized with their natural exchange ions present. Microbial attack on natural soil organic matter and on the bitumen component in the specimens, also reduction of iron constituents from the ferric to the ferrous form was observed in the moist specimens, especially those saturated with Ca- and Mg- exchange ions.

3. Influence of the Character of the Bitumen

Best stabilization results were obtained with standard road tars,

followed by the cracked asphalt cutbacks, the standard steam or vacuum refined cut-back asphalts, and finally the low temperature tars. In the series of uncracked asphaltic cutbacks, the effectiveness of waterproofing increased with increasing asphaltene content. These results are in line with the use of the bitumen as a waterproofing agent, based on chemical or surface chemical reactivity in films too thin to serve as an actual physical coating with cementing properties. The quality series would be quite different if the bitumens had been used not for the waterproofing of cohesive soils, but as thicker bonding films in bituminous concrete, macadam or sheet asphalt.

All the specimens tested had been prepared with water as one of the original components in an amount that, together with the added cutback bitumen, produced a plastic, easily molded material. Then the specimens were air-dried to constant weight before they were submitted to water immersion and strength tests after different periods of immersion. Previous experience had proven that specimens thus prepared not only possessed higher mechanical strength after drying, but also took in less water in the immersion tests than specimens molded of dry soil and cutback bitumen alone. Evidently, even after air drying, the mechanical strength of the specimens was due to the greatest extent to water-films cementing the mineral particles together. It was these films that were protected by the dispersed bitumen from growing too thick and losing their cementing power when the specimens were immersed in water.

There exists already a large literature - especially patent literature - about additives to normal bituminous materials which have the purpose of increasing the affinity of the bituminous materials for the surface of the soil

minerals. These are mainly organic derivatives of ammonia, also fatty, resinous, naphthenic and other organic acids and their salts with bi- and trivalent metal ions, and all sorts of related organic substances composed of relatively large molecules that possess marked electric polarity and surface-chemical activity. Only a few of the many patented additives have found their way into practice and some of the latter have shown a rather rapid loss of their beneficial action when incorporated in road structures.

Coordinated change of both mineral surfaces and bituminous composition is usually performed by substituting Al- or Fe- ions for the naturally occurring exchange ions and by adding organic acids of high molecular weights or their alkali salts to the bitumen.

Most of the recommended additives result in a marked improvement of bitumen treated soil systems, if the latter are tested for strength after the normally employed short-time (usually 7 days or less) complete or partial submersion in water. There are, however, cases on record in which the actual improvement in road performance was much less than indicated by the laboratory test results and sometimes the systems with additives behaved worse on the road than those without.

The fact that short-time laboratory tests on stabilized soil systems may fail to reveal their inadequacy under actual service conditions may be due to one or more of the following causes:

(a) the times for which the test specimens are exposed to attack by free water are much too small, in view of the usually low permeability of clay soil and the low wettability imparted by the bitumen treatment, to permit the specimens to reach those moisture contents which they would obtain ultimately under service conditions; (13.7)

(b) most test methods (except for the freeze-thaw test in portland cement stabilization) make no provisions for the types of water conduction that occur in both the vapor and film phase as a result of temperature differences within the system and that are of great importance under natural conditions of exposure;

(c) microbial decomposition of bituminous and natural soil organic matter can be of considerable practical importance especially in Ca-saturated soil systems. Adjustment of the microbes, surviving the stabilizing treatment to the new environmental and food supply conditions may require several weeks of incubation time.

Whenever microbes play the role indicated under (c), the test methods must be modified or supplemented as follows:

1. Taking and storing of the soil samples for the manufacture of test specimens in a manner that the natural microbe population is largely maintained;
2. preliminary selection of bacteri- and fungicidal additives or methods on the basis of the chemical and physico-chemical properties of the soils and the chosen water repellent bitumen;
3. final selection and dosing of microbe killing admixtures or processes on the basis of laboratory investigations in which conditions favorable for microbial activity are maintained for at least four weeks.

13.15 Additional Physico-Chemical Considerations

It has been pointed out previously that admixture of iron and aluminum salts, which results in substitution of Fe^{+++} and Al^{+++} cations for the natural cation cover of the soil minerals, greatly facilitates the stabili-

zation of heavy clay soils. Such salts are often available as waste materials in the vicinity of steel plants and catalytic organic industry. On the other hand, several types of organic molecules of high molecular weight have been recommended and used as additives for bituminous materials. It is, of course, best if the substances added to the bitumen combine with inorganic components of the mineral surfaces to form water repellent compounds that are strongly anchored in the mineral surfaces by one or more primary valence bonds. For optimal selection of such reactive additives, it is necessary to know as much as possible of the surface chemical characteristics of the soil minerals and especially the counterions of the negatively charged clay minerals. A general scheme for such selection is shown in Table 13-3. The indicated complementary chemicals can be added in small amounts (0.5 - 2%) to low priced organic waterproofing and cementing agents such as ordinary tars and liquid asphalts. Under special circumstances, these additives may be used without the bitumen vehicle.

13.16 Waterproofing of Clay Soils by Addition of Very Small Amounts of Highly Active Substances.

The fundamental principle for rational waterproofing soil stabilization is to maintain at least a portion of the normal water film induced cohesive strength and protect the soil system against excessive water intake. It is known from the effective use of air-entraining agents in portland cement concrete that relatively small amounts of surface active substances may impart great resistance to wetting and capillary water intake by porous inorganic building materials. A cohesive soil that has been made water repellant through the admixture of very small amounts (usually less than

Table 13 - 3

General Scheme for Selection of Additives

Suitable for Different Pedologic Soil Types

Character of Internal Soil Surface	Complementary Substances
1. Conplex Fe- and Al-silicates with $SiO_2/(Al_2O_3 + Fe_2O_3)$ ratio > 2. The clay particles are predominently negatively charged. (Podsolic Soils)	Organic cations usually derived by substituting organic radicals for one or more hydrogens in NH_4OH; also in the case of acidic soils that have reactive Al- and Fe-ions, soaps and high molecular weight organic acids.
2. Clay minerals having SiO_2/R_2O_3 ratios < 2 with or without admixtures of impurities of complex hydrous oxides of Fe and Al. Typical for hot and moist climates. Increase in Al_2O_3 and Fe_2O_3 leads to lowering of the negative and increase in positive charges on clay mineral surfaces.	The positively charged spots on the clay mineral surfaces react with the negative organic anions of fatty, resinous and other high molecular weight organic acids and soaps. The high temperatures and the presence of iron compounds favor oxydation of organic stabilizers, hence use of antioxidant additives is desirable if not necessary.
3. Presence of rather stable secondary soil aggregates covered with humus films rich in lignin, protein and wax-like substances. Typical for Chernozem and related semi-arid soils.	Substances which (a) react with the soil organic matter to produce water-repellant synthetic resins or resin cemented filled plastics. (b) possess microbe killing properties such as the aniline-furfural combinations already developed.
4. Desert, salt and alkali soils, typical for climatic and environmental conditions in which evaporation equals or exceeds precipitation.	Admixture of two or more chemicals in liquid or solution form that are able to form water repellant strong cementation films irrespective of the pH and the salt content of the system. (Certain aniline-furfural combinations)

1%) of organic substances owes its cohesive strength to its thin water films. The small amounts of additive used and the practical realities of soil comminution, mixing and compaction render it impossible to provide a water repellant cover over the entire internal surface of the system. What is formed are water repellant barriers at strategic locations in the system. These barriers are not so much plugs, but rather discomtinuous surface films or rather film patches. Liquid water without hydraulic pressure cannot pass these barriers, but water molecules can do so in the vapor phase and can be condensed again behind the barrier. There they are in a position to increase the thickness of the cohesion-giving water films and thereby to reduce the mechanical strength of the system. Under especially severe conditions, this strength may fall below the minimum requirements for stability in service. Also, liquid water, if under sufficient hydraulic pressure, can slip over the water repellant barriers. These facts and considerations show the natural limitations of waterproofing treatments with very small amounts of additives. Except for soil systems that possess dependable granular bearing skeletons such as waterproofed clay mortar or clay concrete, cohesive soils waterproofed with very small amounts of surface active chemicals should not be used under pavement and surface layers that possess lower water vapor permeabilities than the treated soil. Otherwise, detrimental water accumulation will ultimately take place in the presumably stabilized soil, which then becomes mechanically unstable. However, when left open to the atmosphere, such waterproofing may be quite valuable and economical for time limited civilian and military purposes.

13.17 Volume Relationships in the Stabilization of Silt-Clay Soils

It has been pointed out previously that the water affinity and

susceptibility to stabilization of silt-clay soils depend largely on the surface chemical properties of their constituent particles. This does not mean that phase volume relationships are of no importance. As a matter of fact, such relationships are important in several different ways. First, there are threshold values for different stabilizing agents below which they have very little or no stabilizing power. Second, there exist maximum values for bitumen admixtures which may not be exceeded if the systems are not to become liquid at the higher ranges of service temperatures. Also, the ratio of the liquid phase volumes (water + bitumen) to the phase volume of the soil solids determines whether the system is essentially in the solid or liquid state with the plastic range straddling the transition from one to the other. Within the plastic and the highly viscous liquid range, the shear resistance of a silt-clay soil is usually an inverse logarithmic function of the moisture content. For this reason, in the testing of the efficiency of soil stabilization, water absorption measurements can often be used instead of the more time consuming and destructive testing for shear resistance or compressive strength.

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PROBLEMS

1. Give four different examples of soil stabilization and point out what particular soil property is being stabilized.
2. Show in three examples the connection between the AASHO soil classification for subgrade materials and stabilization for base construction.
3. Explain why a gradation designed for optimum workability, as in the case of portland cement concrete, is not the most suitable for clay concrete.
4. Expressing the gradation of a gravel-sand mixture by the equation

   $p = 100\ (d/D)^m$ in which

   p = percent passing a given sieve with openings of width d

   D = maximum size of aggregate, and

   m = variable exponent, called gradation index, and having one material with m = 0.4 and another with m = 0.5, which would you consider more suitable for bituminous and clay concrete and which for portland cement concrete? Give reasons for your decision.
5. Give two examples each for inorganic and organic cementing materials and explain the molecular mechanism on which their cementing action is based.
6. Under what circumstances will the granulometry of the cementing materials interfere with the packing of the soil particles to be cemented. Illustrate for the case of a sand with maximum size of 1 mm. and portland cement of normal fineness.
7. Describe the structure of a silt-clay soil stabilized by means of portland cement.
8. Explain why water is an important ingredient in the stabilization of silt-clay soils by means of bituminous materials.

9. What stabilization procedures would you consider if you had to stabilize, for base construction, a chernozem soil containing 5% of natural organic matter. Give physical and chemical reasons for your considerations.
10. Explain with examples the role played by bacteria and fungi in stabilization of soild for base construction.

APPENDIX A

PRINCETON UNIVERSITY
Department of Civil Engineering
Soil Stabilization, Engineering 501 (409)

Laboratory Exercise II

1. Calculate percentage of different size fractions of gravel and sand required to make a workable mixture of high density with maximum aggregate size of 1" and minimum size of 0.0058" according to the Rothfuchs relation:

$$p = 100 \frac{\sqrt{d} - \sqrt{d_{min}}}{\sqrt{D} - \sqrt{d_{min}}}$$

where: p = per cent passing sieve with opening d

D = maximum diameter of aggregate

d_{min} = minimum diameter.

The size fractions employed are those corresponding to the sieve set used for determination of the Abrams fineness modulus (Ref. Handbook 53, 1962 Edition "Testing Sieves and Their Uses," W. S. Tyler Company, Cleveland 14, Ohio). See Table II-1 below:

Table II-1. Typical Sieve Analyses and Fineness Modulus of Aggregates

Sieve Designation		Size of openings		Examples Cumulative percentages retained		
Tyler	U.S.	mm	inch	Fine aggregate	Coarse aggregate	33% fine + 67% coarse
100 mesh	100	0.149	0.0058	94	100	98
48 "	50	0.297	0.0116	80	100	93
28 "	30	0.595	0.0232	52	100	84
14 "	16	1.19	0.046	30	100	77
8 "	8	2.38	0.093	12	100	71
4 "	4	4.76	0.185	2	98	66
3/8 inch	3/8	9.51	3/8	0	80	53
3/4 "	3/4	19.0	3/4	0	42	28
1 1/2 "	1 1/2	38.1	1 1/2	0	0	0
			Total	270	720	570
			Fineness Modulus	2.7	7.2	5.7

The fractions of interest for our purpose are accordingly the following: 1# - 3/4"; 3/4" - 3/8"; 3/8" - #4; #4 - #8; #8 - #16; #16 - #30; #30 - #50; #50 - #100.

Instead of calculating the amounts smaller than a certain sieve size by means of the Rothfuchs equation, one can determine this graphically by plotting % passing on the ordinate and the square root of the size opening on the abscissa and drawing a straight line through the coordinate pairs $y = 0$; $x = \sqrt{d_{min}}$ and $y = 100$; $x = \sqrt{D_{max}}$. The ordinate or per cent passing can then be read for any specific size. The difference in the ordinate values for any two sizes is the percentage of fraction lying within the respective size range. Use this procedure to check the values calculated directly with the Rothfuchs equation. Make this graph Fig. 1 of your report.

2. Make up a Rothfuchs gradation mixture of about 70 lbs. total. Fill a 1/2 cu.ft. measure with this mixture placing the material in 3 layers of approximately equal height and rod each layer 25 times with a rounded 3/4" diameter metal rod. In the case of the second and third layers, the rod should penetrate only the uppermost layer during the rodding procedure.

From the weight of the filled and empty container calculate the rodded weight per cu.ft. Taking a value of 2.5 for the specific gravity of the aggregate (unless another value is furnished to you or has been obtained by you in testing the specific aggregate employed), calculate the absolute volume of the solid aggregate in cu.ft/cu.ft. of bulk volume occupied and also the absolute volume of the pore space. Compare the values obtained with those that can be read from the graph in Fig. 2.

3. Calculate the amounts of different size fractions required to make 1, 3 and 5 cylindrical specimens of 6 inch diameter and 12 inch height.

Size fraction	Lbs. required for 1	3	5 specimens
1" - 3/4"			
3/4" - 3/8			
3/8" - 4			
#4 - #8			
#8 - #16			
#16 - #30			
#30 - #50			
#50 - #100			

4. Calculate for a set of five 6" x 12" cylindrical specimens the amounts of Portland cement and water required to fill the previously calculated void space using a water-cement ratio of five gallons per bag of cement and a specific gravity of 3.15 for the cement.

Sample calculation:

(a) Weight of 1 cu.ft. of water 62.5 lbs.

(b) " " " " " solid cement particles = 62.5 x 3.15 = 197 lbs.

(c) " 1 bag of cement = 94 lbs. with solid volume = 94/197 = 0.477 cu.ft.

(d) 1 gal. = 0.1337 cu.ft.

5 gal. - 0.668 cu.ft.

(e) Ratio of absolute volumes of water and Portland cement for 5 gals. of water / 1 bag of cement : 0.668/0.477 = 1.4/1.

Assuming that the Rothfuchs mixture has 24% of voids i.e. 0.24 cu.ft/cu.ft., these would have to be filled by volumes of water and cement in the ratio of

1.4/1 which gives 0.14 cu.ft. of water weighing 62.5 x 0.14 = 8.75 lbs.

0.10 cu.ft. of cement weighing 197 x 0.1 = 19.7 lbs.,

required to fill a void space of 0.24 cu.ft.

5. Calculate the amount of water and Princeton red clay required to fill the void space in a set of five 6" x 12" cylindrical specimens, using a ratio of weight of water to that of dry soil of 1 : 5 and a specific gravity of the soil of 2.66.

6. Calculate the respective amounts of Portland cement, dry soil and water required to make specimens, the pore space of which is filled:

(a) 75% with Portland cement plus water (W/C = 5 gal/cu.ft.)
25% with soil plus water (dry soil/water = 5/1 by weight)

(b) 50% with Portland cement and water
50% with soil and water

(c) 25% with Portland cement and water

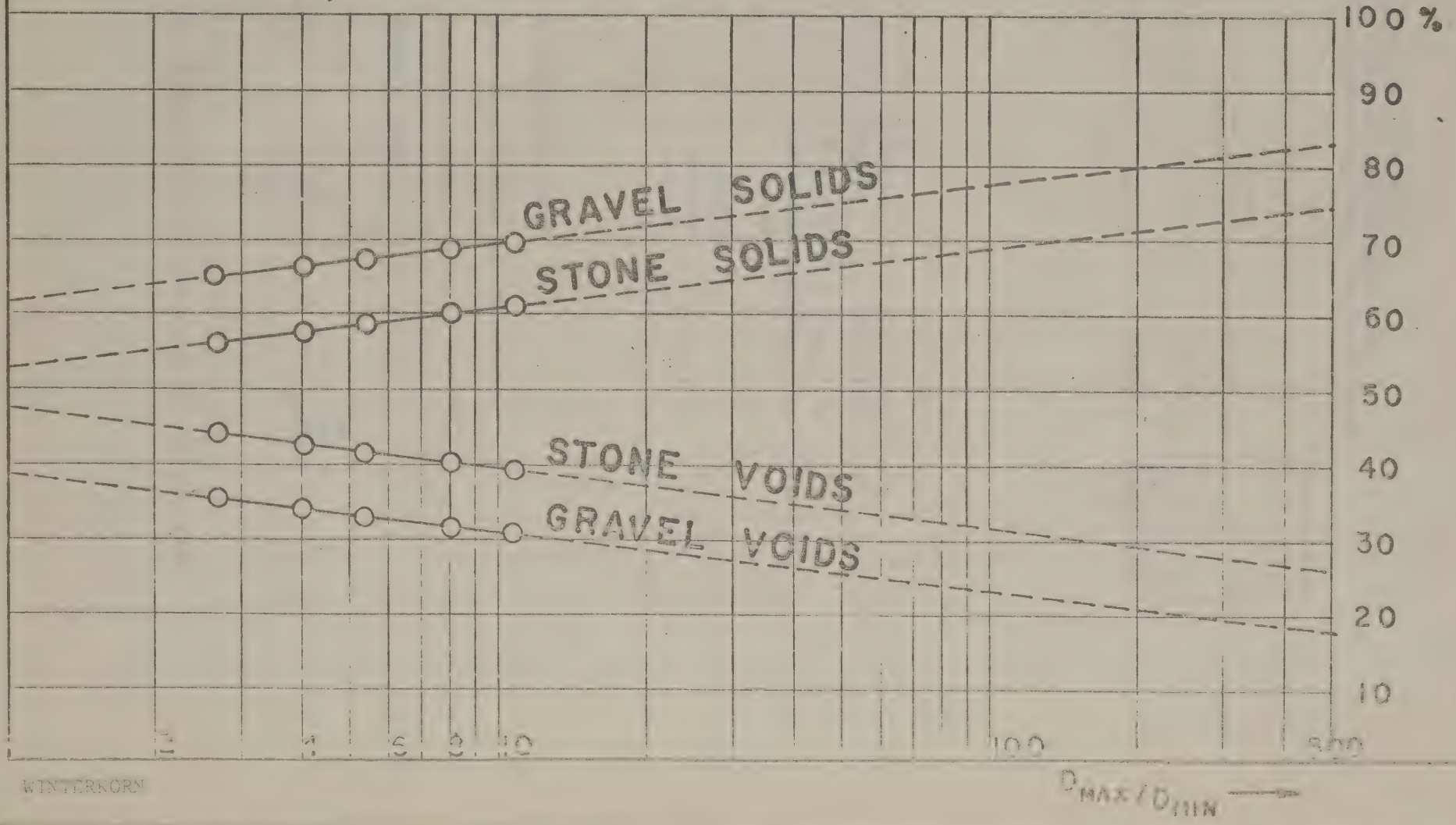
(d) 75% with soil and water

7. Make the same calculations for amounts of dry soil, water and RC-3 asphaltic cutback of proportions of dry soil : water : RC-3 = 10 : 2 : 1.

8. Make the same calculations as in (7) replacing the RC-3 by a combination of 2 parts by weight of aniline to 1 part of furfural. Specific gravity of aniline 1.022; specific gravity of furfural 1.108.

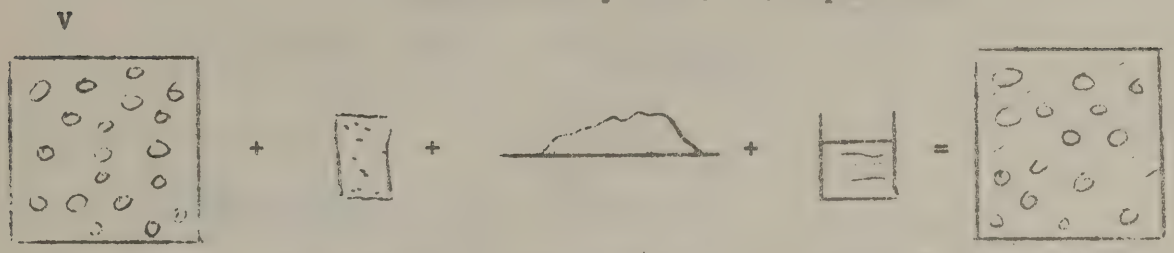
—FIG. 2—

RELATION BETWEEN NORMAL POROSITY AND SIZE RANGE AS EXPRESSED BY D_{MAX}/D_{MIN} IN CONTINUOUS GRADING.

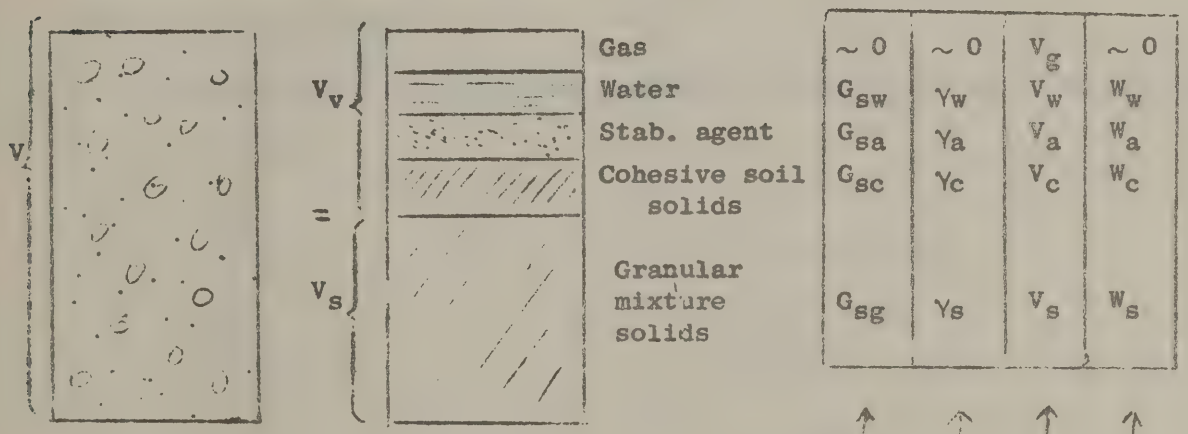


Calculation of Stabilized Soil Mixtures

(ad: Laboratory Exercise 11)
contributed by Prof. Dr. Arpad Kezdi



Symbols and definitions



G_s Specific gravities

γ Unit weights (lbs/cu ft)

V Volumes (cu ft)

W Weights (lbs)

In general: $W = V_\gamma = V\, G_s\, \gamma_w$

Void ratio of the skeleton: $e = \dfrac{V - \frac{W_s}{\gamma_s}}{\frac{W_s}{\gamma_s}}$; $n = \dfrac{V - \frac{W_s}{\gamma_s}}{V}$

It will be assumed that the admixtures fill the voids of the skeleton ($V_g \approx 0$)

Water content of cohesive soil: $w = \frac{W_w}{W_c}$

" " of Stab. Soil: $w = \frac{W_w}{W_c + W_s}$

Water-cement ratio:

$$\alpha = \frac{\text{volume of water}}{\text{volume of cement}} = \frac{V_w}{V_a} \quad ; \quad \frac{W_w}{W_a} = \alpha \frac{\gamma_w}{\gamma_a}$$

Specific amount of stabilizing agent:

$$a = \frac{W_a}{W_s} \qquad \text{or} \qquad \frac{W_a}{W_c}$$

ad 4. Portland cement

The amounts of Portland cement and water required to fill the pore space of the skeleton:

$$W_a = \frac{nV\gamma_a}{1 + \alpha}$$

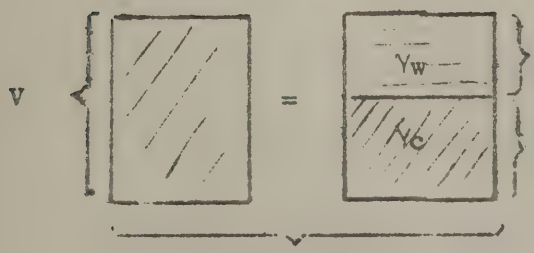
$$W_w = \frac{\alpha n V \gamma_w}{1 + \alpha}$$

$$V_w + V_a = V_v$$

$$\frac{V_w}{V_a} = \alpha$$

$$V_v = nV$$

ad. 5. Clay-gravel



water content of the clay:

$$w = \frac{e\,\gamma_w}{\gamma_c}$$

Unit weight of saturated clay:

$$\gamma = \frac{\gamma_c + e\gamma_w}{1 + e} \cdot = \gamma_c \frac{1 + w}{1 + e} =$$

$$= \gamma_c \frac{1 + w}{1 + w \frac{\gamma_c}{\gamma_w}} = \gamma_c \frac{1 + w}{1 + G_{sc} w}$$

Weight of wet clay to fill the voids:

$$W = \gamma nV$$

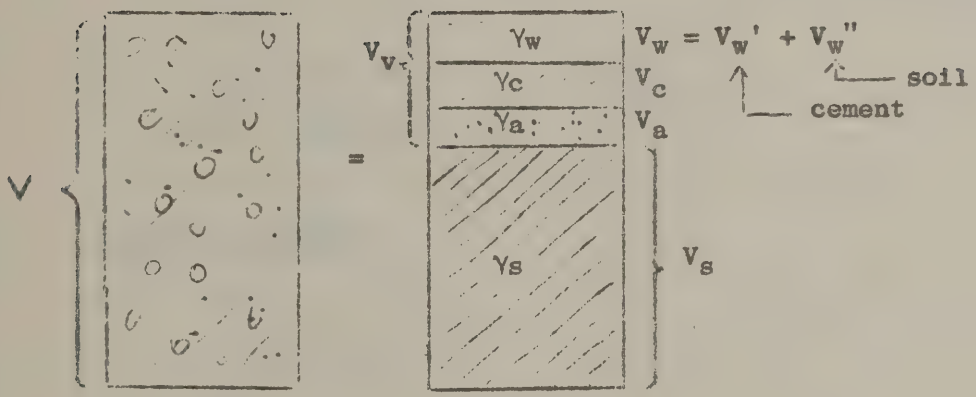
Dry weight of clay:

$$W_c = nV \frac{\gamma_c}{1 + G_{sc}{}^w}$$

Weight of water:

$$W_w = nV \frac{{}^w\gamma_c}{1 + G_{sc}{}^w}$$

ad 6.



Volume of cement + water: $\beta V_v = \beta nV$
($\beta = 0.25;\ 0.50;\ 0.75$)

$V_a + V_w' = \beta nV$

$$V_a = \frac{\beta nV}{1 + \alpha}$$

$W_w'/V_a = \alpha$

Weight of cement:

$$W_a = \frac{\beta nV}{1 + \alpha} \gamma_a$$

Volume of clay soil + water: $V_v - \beta V_v = (1 - \beta)nV$

$$\frac{\text{Volume of water in clay}}{\text{Volume of clay solids}} = w \frac{\gamma_c}{\gamma_w}$$

$$\left.\begin{aligned} V_c + V_w'' &= (1 - \beta)nV \\ \frac{V_w''}{V_c} &= w\,\frac{\gamma_c}{\gamma_w} \end{aligned}\right\}$$

Weight of dry clay

$$W_c = \frac{(1 - \beta)nV}{1 + G_{sc}w}\,\gamma_c$$

Weight of water:

$$W_w = (V_w' + V_w'')\gamma_w = \alpha\,\frac{\beta nV}{1 + \alpha}\,\gamma_w + \frac{(1 - \beta)nV_w\gamma_c}{1 + wG_{sc}}$$

$$W_w = \gamma_w nV\left[\frac{\alpha\beta}{1 + \alpha} + \frac{(1 - \beta)wG_{sc}}{1 + wG_{sc}}\right]$$

If $\beta = 1$ → Case 4.

$\beta = 0$ → Case 5.

Sample calculation

ad 6. (4,5)

γ_w = 62.5 lbs/cu ft

n = 0.26

V = 0.5886 cu ft (3 specimens)

w = 0.20

G_{sc} = 2.66

α = 1.4

$$W_w = 62{,}5 \cdot 0{,}26 \cdot 0{,}5886\left[\frac{1.4\beta}{2.4} + \frac{0{,}2.2{,}66(1 - \beta)}{1 + 0{,}2.2{,}66}\right]$$

$$= 9{,}55\,[0{,}584\beta + 0{,}346(1 - \beta)]$$

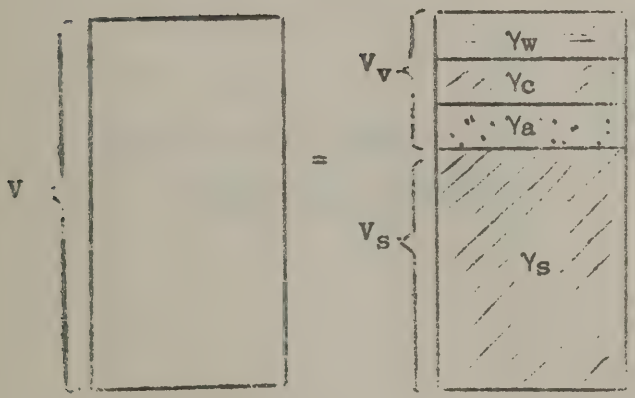
$$= 2{,}27\beta + 3{,}3$$

β	2.27 β	Water W_w lbs		Cement W_a lbs	Clay W_c lbs
0	0	3.3	→ 5.	0	16.6
0.25	0.57	3.87		3.13	12.45
0.50	1.13	4.43	6.	6.25	8.3
0.75	1.70	5.00		9.4	4.15
1.00	2.27	5.57	→ 4.	12.5	0

$$W_a = \frac{\beta \cdot 0{,}26 \cdot 0{,}5886}{1 + 1.4} \cdot 3{,}15 \cdot 62{,}5 = 12.5\ \beta$$

$$W_c = \frac{(1 - \beta) \cdot 0{,}26 \cdot 0{,}5886}{1 + 0{,}2 \cdot 2{,}66} \cdot 2{,}66 \cdot 62{,}5 = 16{,}6\ (1 - \beta)$$

ad 7. <u>Asphaltic cutback - clay - gravel</u>



V_w → water
V_c → cohesive soil
V_a → asphaltic cutback

→ skeleton

$$w = \frac{V_w\gamma_w}{V_c\gamma_c} = \frac{W_w}{W_c} \qquad a = \frac{V_a\gamma_a}{V_c\gamma_c} = \frac{W_a}{W_c}$$

Unit weight of the mixture:

$$\gamma = \frac{W}{V} = \frac{V_w\gamma_w + V_c\gamma_c + V_a\gamma_a + V_s\gamma_s}{V}$$

Volume of voids:

$$V_v = nV = \frac{W_w}{\gamma_w} + \frac{W_c}{\gamma_c} + \frac{W_a}{\gamma_a} \qquad W_w = wW_c$$

$$= W_c \left(\frac{w}{\gamma_w} + \frac{1}{\gamma_c} + \frac{a}{\gamma_a} \right) \qquad W_a = aW_c$$

Weight of dry soil (clay):

$$W_c = \frac{nV}{\frac{w}{\gamma_w} + \frac{1}{\gamma_c} + \frac{a}{\gamma_a}}$$

Weight of water:

$$W_w = w\, W_c$$

$$W_a = a\, W_c$$

ad 8.

Calculation the same as with 7.

$$\gamma_a = \frac{2\,\gamma_{anilin} + \gamma_{furfural}}{3}$$

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